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Near Critical CO2 Extraction of Hazardous Organics from Acrylonitrile Pesticide and Steel Mill Wastes

Critical Fluid Systems, Inc., Cambridge, MA

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NEAR CRITICAL CO_2 EXTRACTION OF HAZARDOUS ORGANICS FROM ACRYLONITRILE, PESTICIDE AND STEEL MILL WASTES

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An extractor plate efficiency was determined based on the Kremser-Souder-Brown equation using the results of the acrylonitrile waste runs. This efficiency was used to design a commercial scale extractor. A conceptual design for a commercial scale process is also presented.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report presents the results of a study which examined the use of near critical carbon dioxide to extract hazardous organics from industrial wastes. Three types of wastes were treated; a waste stream from an acrylonitrile plant, an oily sludge from a steel mill plant and a slurried sludge from a pesticide manufacturing plant. Industries producing wastes similar to those listed here will find this report useful when assessing the viability of waste treatment methods. For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

Near critical carbon dioxide was used to extract hazardous organic chemicals from three aqueous waste streams in a pilot plant scale continuous liquid-liquid extraction system. Extractions were performed on waste streams representative of actual streams from steel, pesticide, and acrylonitrile manufacturing plants.

An extractor plate efficiency was determined based on the Kremser-Souder-Brown equation using the results of the acrylonitrile waste runs. This efficiency was used to design a commercial scale extractor. A conceptual design for a commercial scale process is also presented.

This report was submitted in fulfillment of Contract Number 68-03-1956 by Critical Fluid Systems, Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from December 4, 1984 through March 28, 1986, and work was completed as of May 9, 1986.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

BMDL	--	Below Minimum Detection Limit
CV	--	Control Valve
ft	--	feet
gal	--	gallons
GC	--	Gas Chromatograph
gph	--	gallons per hour
gpm	--	gallons per minute
hr	--	hour
Kremser Equation	--	Kremser-Brown-Souder Equaton
kw-hr	--	kilowatt-hour
lb	--	pound
MBC	--	Material Balance Closure
ml	--	milliliter
MPa	--	mega Pascal
NCL	--	Near Critical Liquid
ND	--	Non-detectable
ppm	--	parts per million
psi	--	pounds per square inch
psig	--	pounds per square inch gauge
SCF	--	Supercritical Fluid
S.D.	--	Standard Deviation
solvent-to-feed ratio	--	solvent rate in mass units per unit time divided by the feed rate
wt.%	--	weight percent
xylene	--	Indicates the use of mixed xylenes (ortho, para and meta)

SYMBOLS

CO_2	--	carbon dioxide
^oC	--	degrees Celsius
E	--	sieve tray efficiency
^oF	--	degrees Fahrenheit
$\sum$	--	sum of
g/cm^3	--	grams per cubic centimeter
m	--	distribution coefficient
N_{th}	--	theoretical number of extractor trays
N_{act}	--	actual number of extractor trays
P	--	pressure
pH	--	negative log concentration of hydrogen ions
Q	--	S/F x m
S/F	--	solvent-to-feed ratio
T	--	temperature
X	--	mean
X_f	--	weight fraction in the feed
X_r	--	weight fraction in the raffinate
X_i	--	individual observation
Y_s	--	weight fraction in the incoming solvent
"	--	inches
'	--	feet

SECTION 1

INTRODUCTION

NEAR CRITICAL LIQUIDS AND SUPERCRITICAL FLUIDS AS SOLVENTS

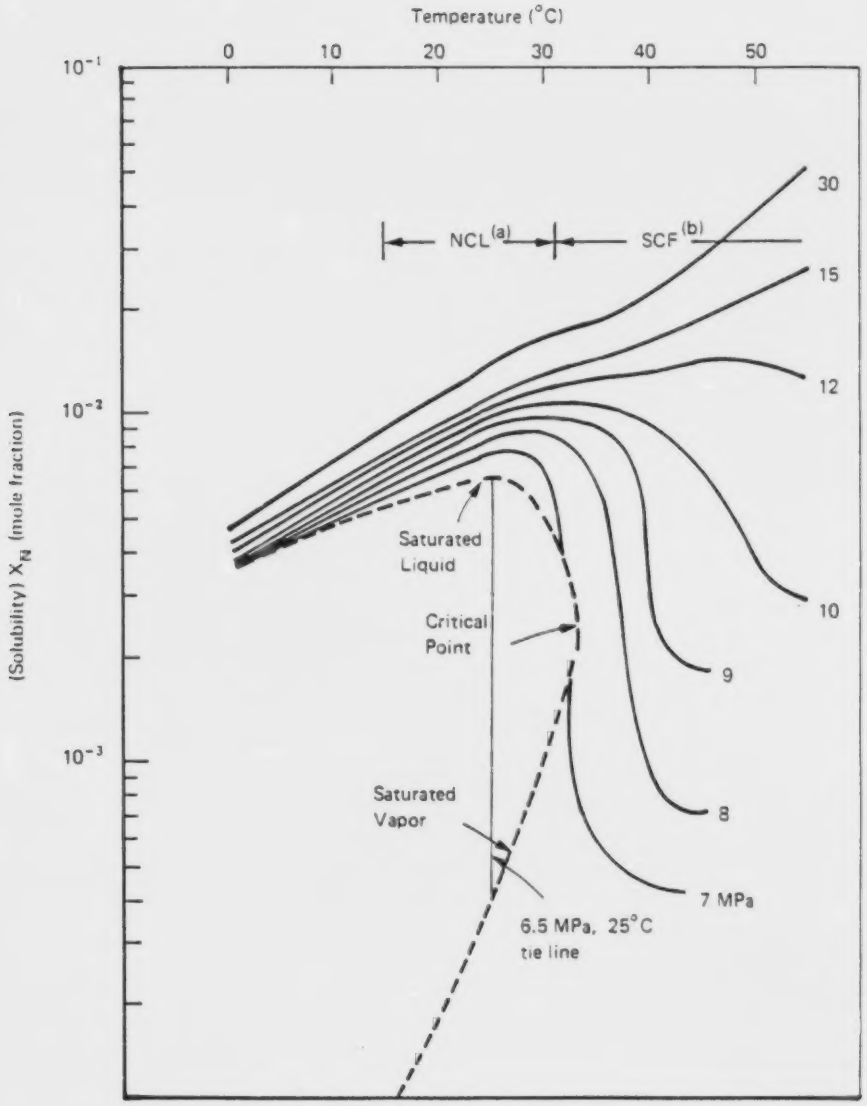
The use of near critical liquids and supercritical fluids as solvents for extraction has been of interest for at least 20 years. Successful applications have been developed where the economic gains offset the costs of high pressure operation. Two components of that gain are:

1. Credits for by-product recovery.
2. Reduced processing costs.

A "critical fluid" is a fluid near its thermodynamic critical temperature and pressure. At the critical point there is no distinct liquid or vapor state. The various properties of the fluid in this state (e.g., density, viscosity, diffusivity) are intermediate between the corresponding values of the fluid in the gas and liquid states. Further, these properties are not fixed. They can be varied by manipulating temperatures and/or pressures. Not only are these physical properties variable above the critical point, so also are the solubilities of organic solutes. This can be observed in Figure 1, a solubility map of naphthalene in near- and supercritical carbon dioxide. This diagram is based on published solubility data in the near-critical region[1] taken with data on the solubility of naphthalene in saturated CO_2[2]. We see in this diagram fairly conventional solute behavior in the region of 0 to 25 C. Solubility increases with increasing temperature and, at a given temperature, however, we observe markedly different behavior. At pressures near the critical pressure (7.5 MPa) the solubility sharply decreases with increasing temperature. The effect becomes less pronounced as pressure is increased, but it is clear that near the critical pressure solubility is a strong function of temperature. Thus, we see that operation in the near critical and supercritical regime allows the process designer to tailor the solvent to the particular extraction under consideration.

A number of fluids have been proposed for use as extraction solvents. Some of these fluids have been listed in Table 1 along with their critical properties. Carbon dioxide is a prime candidate for organic aqueous waste extraction and was chosen for this project. Carbon dioxide is inexpensive, relatively safe and can be used at near ambient temperatures.

The scope of the wastes examined on this project was extremely broad. Waste streams from acrylonitrile, steel and pesticide manufacturing plants were extracted with critical carbon dioxide. The common feature to the three wastes extracted was the presence of a 70% by weight or greater water fraction. Two of the



(a) NCL = Near Critical Liquid

(b) SCF = Supercritical Fluid

FIGURE 1 SOLUBILITY OF NAPHTHALENE IN CARBON DIOXIDE NEAR ITS CRITICAL POINT

1 atm. = .1013 MPa

wastes had solids present in the feed which added to the complexity of operation and data interpretation. In all three, the focus of experimentation was to efficiently recover specific organics from the bulk of water present. This report tells of the results of this project and suggests solutions to the problems of treating these hazardous wastes using critical carbon dioxide as an extraction solvent.

TABLE 1. CRITICAL PROPERTIES FOR SELECTED FLUIDS

FLUID	CRITICAL TEMPERATURE (Tc, ^{o}C)	CRITICAL PRESSURE (Pc, MPa)	CRITICAL DENSITY (Pc, g/cm^3)
Pentane	296.7	3.4	0.232
Butane	152.0	3.8	0.228
Solvent-12	112.0	4.1	0.558
Propane	96.9	4.3	0.220
Ethane	32.3	4.9	0.203
Ethylene	9.9	5.2	0.227
Carbon Dioxide	31.1	7.5	0.468
Sulfur Dioxide	157.6	8.0	0.525
Ammonia	132.4	11.	0.235
Water	374.3	22.	0.326

OBJECTIVE

The primary objective of this pilot plant program was to demonstrate the technical feasibility of the critical fluid extraction of hazardous organic chemicals from aqueous waste streams. This was achieved by gathering engineering data and then evaluating the effectiveness of the extraction process.

This report presents the pilot plant experimentation, a full description of the process, equipment, operating procedures, and the data obtained from experimental runs. The results of the experimentation and an analysis are presented which were used to demonstrate the technical feasibility of the process and to design a more detailed commercial system.

Prior evaluations of this critical fluid process to extract organic components from aqueous solutions have been based on engineering analyses and designs which drew from a body of literature[3]. Our pilot plant represented the first effort to demonstrate the use of continuous counter-current critical-fluid-liquid extraction combined with solvent recovery utilizing a vapor recompression cycle. The pilot-plant equipment was designed to permit scale-up to industrial capacities. Thus, the information gathered from the pilot plant would be applicable to the preparation of a commercial design, and technical success of the pilot plant could be translated into technical feasibility of a commercial-scale plant as done in Section 6.

The pilot plant provided data for economic evaluations based on feeds and conditions actually tested. In addition, if there were satisfactory agreement between pilot-plant data and engineering models, the models could be used with greater confidence for cases not studied in the pilot plant.

HAZARDOUS AQUEOUS WASTE STREAMS

Steel Mill Sludge Waste Streams

The steel mill industry produces a variety of wastes which are potential candidates for treatment with the critical fluids extraction process. The deoiling of mill scale has been previously studied[4]. Steel mill sludge, a collective waste stream, is another candidate which is studied in this report.

The sludge comes from the underflows of a two-stage clarification process. The underflow from a first stage clarifier is sent to a second stage for additional residence time for gravity separation. The final sludge waste is drawn from the bottom of this second stage.

The sludge contains oil, water, iron fines, and toxic and non-toxic residues. The solids to water ratio is approximately 30 to 70 by weight. Oil and grease content can vary between 6 to 30% of the weight of the solids which was measured as weight loss on ignition of the dry solids.

One plant can produce 50,000 wet tons per year of this sludge waste. From an economic standpoint, the industry is looking

to recover as much oil as possible for its fuel value or for use as a recycled lubricant. Also, once the water and oil are eliminated, iron may also be recovered by magnetic separation. From an environmental standpoint, the industry would be able to significantly reduce its landfill capacity and also to detoxify residues for landfill more effectively.

Pesticide Waste Streams

The second steam tested was a simulated waste stream from a pesticide manufacturing plant. The stream originated from a variety of sources in the process which are pumped in a slurry over to a decanter tank where the slurry separates into three layers.

The top or light portion (5% of the total volume) contains mostly xylol (mixed xylenes), some suspended solids and carbon tetrachloride. This layer is separated into a light slops tank and sent to an incineration facility. The bottoms (5% of the total volume) is a sludge containing solids, salts, carbon tetrachloride and other insolubles. These are collected and sent to be treated. The middle layer (90% of the total volume) is aqueous and contains organics at levels above their normal solubility limit due to the presence of soaps or surfactants and suspended solids fines. This aqueous portion is sent to a biotreatment facility which requires that there be no free organics present or in other words, the organics level must be at or below its solubility limit in water.

Extraction of the organics from the pesticide waste stream could provide two benefits. First, carbon tetrachloride is toxic to the bacterial cultures present in the biotreatment facility. Removal of this organic would greatly enhance the efficiency of the process on treating the other organics. Second, solvent recovery could present a potential cost savings and also enhance biotreatment of the aqueous waste layer.

The feed stream used to simulate the pesticide waste stream described above composed of 6.0% mixed xylenes, 1.0% carbon tetrachloride, 5.0% of the bottoms sludge and the remaining 88.0% being water, all on a weight percent basis. The purpose of testing this feed was to explore critical fluids extractions capability in significantly reducing the level of carbon tetrachloride in the aqueous stream and in recovering mixed xylenes from both the light slops and the aqueous layers of the waste feed.

Dissolved Organics Waste Streams

The third stream tested was a simulated waste stream from an acrylonitrile manufacturing plant. The stream consists of predominantly dissolved organics. The current method of waste disposal for this stream is deep-well injection. If deep-well

regulations are changed, detoxification may be necessary. Stripping is not a viable alternative for treating on the order of 125 gpm of dilute waste, as the amount of heat necessary to remove the organics from the water would make the process too costly.

Extraction of the toxic organics from this waste stream could provide the following benefits. First, it would allow bio-treatment in lieu of deep-well injection. Second, it would provide significant reduction in toxicity of deep-well streams. Third, it would isolate toxic elements which could be incinerated at acceptable costs. And finally, the additional recovery of acrylonitrile product would represent a significant economic gain.

The industrial stream consists of the toxic organics, acrylonitrile (250 ppm), acetonitrile (350 ppm), hydrogen cyanide (500 ppm), and non-toxic organics, ammonium ferrors and sodium sulfates (2.5 wt %). The simulated waste used for testing did not contain hydrogen cyanide due to permitting restrictions. The purpose of testing this feed was to explore critical fluid extractions ability to significantly reduce the level of toxicity in the primarily aqueous stream from 0.1 - 1.5 % toxicity to the parts per million level.

SECTION 2

SUMMARY AND CONCLUSIONS

STEEL MILL SLUDGE WASTE

The steel mill industry produces a variety of wastes which are potential candidates for treatment with the critical fluids extraction process. Sludge coming from the underflow of a two-stage clarification process which contains oil, water, iron fines and residues was one of the wastes run with carbon dioxide solvent in this project. The focus of this experimentation was to recover oil from the sludge by extraction.

Extracting oil from the steel mill sludge waste with carbon dioxide in the pilot plant extraction system was difficult. Major plant design modifications were necessary to handle a waste feed with such a high loading of abrasive solids. After the adjustments were made, experimentation proceeded with results given in Table 2 of Section 5.

Dilution of the feed before processing was attempted with the hope of preventing valve blockage due to the 2-5% particulate loading. However, this was found to have a negligible effect on the performance of the extraction system. Solvent-to-feed ratio was varied to find an optimal oil recovery. Using a 4.6 to 1.0 solvent-to-feed ratio by weight, an oil reduction of 30% was achieved. Higher solvent-to-feed ratios did not enhance oil recovery significantly.

Commercial systems would have to operate at or above the 4 to 1 solvent-to-feed ratio to recover enough oil for an effective extraction with carbon dioxide. The cost of operating at this level of incoming solvent must be examined. Maximizing the difference between the fuel value of oil recovered and the cost of fresh solvent is necessary to make the process more economically viable. Finally, commercial systems would have to be designed to handle the abrasive slurry. A mix settler or stirred tank extractor would be more effective than a sieve-tray extractor for this type of feed.

PESTICIDE WASTE

The second waste tested was from a pesticide manufacturing plant. The waste was a slurry which when separated by decantation contains a top layer (mostly xylene), a middle aqueous layer and a heavy bottoms layer classified as a sludge. The waste contains water, xylenes, carbon tetrachloride, solids fines, salts and other insolubles. The purpose of these experiments was to extract carbon tetrachloride and the mixed xylenes from the waste. The mixed xylenes could be recycled, and the carbon tetrachloride is an extremely hazardous chemical which must be isolated.

Pesticide waste was run in the pilot plant extraction system with carbon dioxide as the solvent. Distribution coefficient determinations previously made in a laboratory stirred extractor system indicated that the separation would be easy. (See Section 5) This, however, was not the case in the pilot plant as seen by results listed on Tables 3 and 4 in Section 5. The difference between pilot plant and laboratory scale results are probably due to the high shear mixing present in the laboratory extractor during the extraction process, while there is none in the pilot plant extraction.

The multipass extraction experiment resulted in an 80% overall reduction in the carbon tetrachloride level in the waste. The overall reduction was calculated using the initial feed concentration before the first pass and the final raffinate concentration after the last pass of a four-pass experiment. The experiment was run with primarily a solvent-to-feed ratio of 1 to 1 at a high flow rate of 4.5 lbs-per-minute (used to enhance mixing in the extractor). A significant increase in the extractability of carbon tetrachloride was found in an experiment done in a single pass when the solvent-to-feed ratio was doubled. A 41% reduction was observed for a solvent-to-feed ratio of 2 to 1 and only an 8% reduction for 1 to 1.

Removal of the xylenes was more difficult. At first it appeared as shown in Table 4 of Section 5 that the concentration of xylene in the raffinate was increasing during the multipass experiment. The method employed in performing the multipass extraction, however, led to an explanation of this anomaly. The feed for each pass through the extractor during the multipass experiment is the same body of liquid as the raffinate from the previous pass. Two conclusions can be drawn from this knowledge. First, since the feed concentration of xylenes dropped by 60% over the last three passes, then the raffinate level must have as well. Second, there must have been a decantation or entrapment of xylene in the system at some point between the extractor and the raffinate tank which led into the raffinate sampling system.

A commercial process could focus specifically on reducing the carbon tetrachloride level in the aqueous layer of the waste. This portion is typically treated in a biotreatment facility, and the bacterial cultures are sensitive to chlorinated hydrocarbons. Removal of carbon tetrachloride would significantly enhance the biotreatment facilities overall performance. A commercial process treating the whole waste stream should probably be equipped with a stirred tank extractor due to the presence of multiple phases and solids in the waste feed.

DISSOLVED ORGANICS WASTE

The last waste treated was from an acrylonitrile manufacturing plant. This waste contains acetonitrile, acrylonitrile, salts of sulfates, and water. The focus of experimentation for this waste was to extract acetonitrile and acrylonitrile with carbon dioxide to both detoxify the waste and to recover the acrylonitrile product.

A multipass extraction experiment was conducted with a solvent-to-feed ratio of 1.5 to 1.0. Overall reductions of 99.4% and 99.6% were achieved for acetonitrile and acrylonitrile in just four passes through the extraction system.

The extractor was analyzed using the Kremser equation, and an average sieve tray efficiency was determined (E = .44) assuming a constant distribution coefficient (m = .76). A material balance was performed around the extractor. Closure was basically complete (95%) for the first pass of the experiment but became poor (55%) for later passes due to magnification of error in laboratory analysis at low organic concentrations.

Given the high degree of extractability of the organics from this waste feed at a pilot plant level, a commercial scale extractor was designed and a total process conceptual design was developed for a more concentrated waste stream.

An analysis of the effect of a 10% error in distribution coefficient on extractor sizing indicated that for this system, a corresponding 50% error in the number of trays could be incurred. Future design work must concentrate on accumulating more extensive distribution coefficient data and not assuming a constant distribution coefficient (i.e. using a McCabe-Thiele analysis), when analyzing the extractor's efficiency.

SUMMARY OF CONCLUSIONS

Steel Mill Sludge Waste

Extraction of oil from the waste increased with increasing solvent-to-feed ratio.

Dilution of the feed before extraction had a negligible effect on extractor performance.

An oil reduction of 30% was experienced from an extraction run with a solvent-to-feed ratio of 4.6 to 1.

Commercial processes should operate at a solvent-to-feed ratio greater than 4 to 1 and should be designed to accommodate a high solids load. A stirred tank or mixed settler as opposed to a sieve tray extractor should be used for a feed of this nature.

Pesticide Waste

The multipass extraction resulted in a 80-85% reduction in the level of carbon tetrachloride in the waste. The extraction was run with a solvent-to-feed ratio of 1 to 1.

Extractor performance was significantly effected here by solvent-to-feed ratio changes. In one pass, the reduction of carbon tetrachloride for a 2 to 1 ratio was 41.3% while for a 1 to 1 ratio was only 7.8%.

The multipass extraction resulted in a 60% reduction in xylene. The poor extractor performance here was due to the presence of multiple phases, solids, and soaps or surfactants in the feed.

A Commercial process should focus on the extraction of carbon tetrachloride from only the aqueous phase of the feed. Biotreatment facilities can successfully process the aqueous portion of the waste once the carbon tetrachloride level is reduced to below its solubility limit.

Dissolved Organics Waste

The multipass extraction resulted in a 99.4% and 99.6% reduction in acetonitrile and acrylonitrile levels, respectively. The multipass extraction was conducted with a solvent-to-feed ratio of 1.5 to 1.

An extractor sieve tray efficiency was calculated using the Kremser equation to find the number of theoretical trays. An individual tray efficiency of .44 was found assuming a constant distribution coefficient of 0.76.

A material balance analysis around the extractor was performed for the multipass experiment. Closure was nearly complete (95%) at high concentrations but became difficult at low concentrations (57%). This was due to error in analysis and carryover of organics from one extractor pass to the next.

A commercial scale extractor was designed based on extracting a feed containing 1680 ppm of acetonitrile, 1200 ppm of acrylonitrile, and 2.0 weight % ammonium sulfate. It was determined that a solvent-to-feed ratio of 2 to 1, a reflux ratio of 1 to 1, and 27 trays at 44% efficiency were required to reduce the total toxic organics level to 10 ppm. Extractor sizing was shown to be highly sensitive to errors in distribution coefficient determinations. More complete equilibrium data may be necessary to perform a non-linear McCabe-Thiele extractor analysis.

SECTION 3

GENERAL EXPERIMENTAL APPARATUS AND
OPERATING PROCEDURES

The following procedure was used for the pesticide and dissolved organics waste streams only and does not wholly apply to the steel mill sludge waste streams. Feed-specific modifications of the apparatus are reported in Section 6.

LABORATORY SCALE EXTRACTIONS

To determine a suitable range of solvent to feed ratios for the pilot plant runs, distribution coefficients were evaluated for the three feeds with the solvent carbon dioxide. These coefficients were obtained using a laboratory scale extractor system shown in Figure 2.

The solvent, carbon dioxide in this case, is compressed and fed to the single stage, stirred extractor vessel. There in contact with the feed equilibrium concentrations of the solute are achieved in the extract and raffinate phases. Extract can be collected in the pressurized collection vessel and raffinate can be drawn from the bottom of the extractor.

Listed below is the operating procedure used for distribution coefficient determinations:

1. Prepare approximately one liter of feed if being simulated; record the weight percent of each component.
2. Stir feed to obtain homogeneous mixture, and decant 50 ml. for pH and density determination.
3. Pull vacuum on the extraction vessel.
4. Load vessel with approximately 350 ml. of feed; note the exact volume and mass of feed charged to the vessel.

5a. Pressurize vessel to 20 psig with CO_2 vapor and stir gently for 1 or 2 minutes.

5b. Open raffinate valve to collect 10 ml. of feed and discard.

5c. Open raffinate valve and collect 40 ml. of feed in septum cap vial filling vial to the very top.

6. Pressurize the extraction vessel with liquid CO_2 to attain a pressure of 1200 psi.
7. Check for phase interaction; note the number of phases present.
8. Stir feed and solvent at high speed for 15 minutes. A longer mixing period may be required for complete equilibrium, depending upon the nature of the feed.
9. Allow phases to completely separate (usually 15 minutes is adequate).
10. Open raffinate valve to collect 10 ml. of the aqueous phase, and discard.

11. Open raffinate valve again to collect 40 ml. of the aqueous phase directly into a septum vial, filling vial to the very top.
12. Collect an additional raffinate sample (50 ml.) for pH and density determinations.
13. Depressurize, empty and clean vessel.
14. Repeat steps 3 through 13 to obtain a duplicate data point; do not collect additional samples for pH and density determinations.

Preliminary experiments were performed to determine solubility distribution coefficients for the various feeds. The distribution coefficients were used to choose appropriate solvent to feed ratios for experimental runs. The distribution coefficient (m) is defined by the expression below:

$$m = \frac{\dfrac{\text{Mass of Solute in Solvent Phase}}{\text{Total Mass of Solvent Phase}}}{\dfrac{\text{Mass of Solute in Aqueous Phase}}{\text{Total Mass of Aqueous Phase}}}$$

The stirred extraction vessel shown in Figure 2 was charged to approximately half its total volume with feed and then filled with liquid CO_2 at a pressure of 1200 psi. The extractor's stirrer was run for fifteen minutes and then the phases were allowed to settle for another fifteen minutes. Samples of the feed and raffinate were then taken and analyzed by gas chromatography. Results for the distribution coefficient determinations are given in Section 5 of this report.

PILOT PLANT SCALE EXTRACTIONS

Experimental procedures were the same for all runs. However, modifications of the extraction unit were necessary for the steel mill sludge feed due to the high percentage of particulate loading. Modifications, which are specific to the steel mill sludge runs, are discussed in Section 4.

General Experimental Procedure

The extraction plant was pressurized, and the flow of carbon dioxide was established. Delivery of feed was initiated, and when feed and solvent flow rates stabilized, a desired reflux ratio could be set. Mass flow rates and operating conditions were recorded on a fifteen minute interval basis.

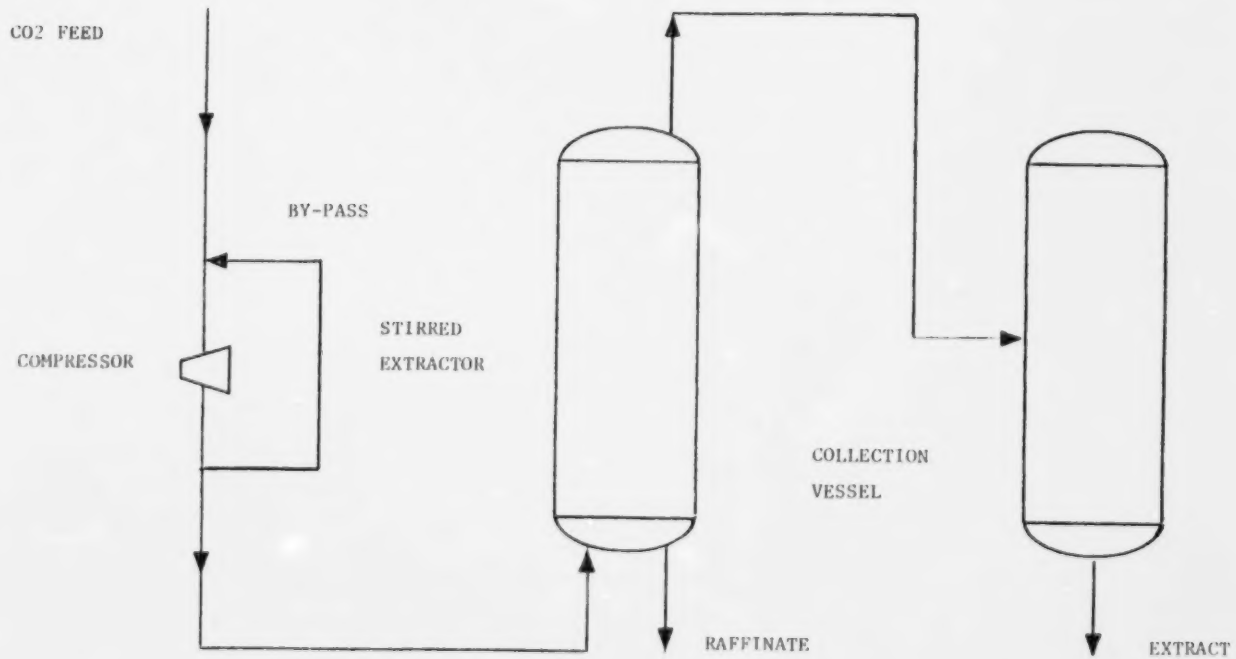


FIGURE 2 - LABORATORY SCALE EXTRACTION FLOW DIAGRAM

Mass flows were determined by using variations on classic bucket and stopwatch techniques. Solvent mass flow was determined using a mass flowmeter equipped with a rate and totalizer readout. The instantaneous rate would fluctuate, but the mass totalized reading, when taken with a panel mounted digital watch, gave very accurate overall mass flows. The flowmeter was the primary sensor for the solvent flow control loop. Setting the loop to hold a 2 lb/min flowrate would consistantly produce the desired flowrate whether averaged over five minutes or two hours.

The aqueous feed was delivered to the extractor using a variable-stroke piston pump. The pump was calibrated (setting vs. delivery) and again, as a second check, the feed tanks were mounted on a balance. The balance was equipped with an alarm that would sound as a preselected weight was passed. The clock time would be noted (to the second) and mass flows calculated. A similarly equipped balance and technique was used for the raffinate tank. Thus, all mass flows, with the exception of the extract stream, were accurately measured.

Samples of feed and raffinate were taken at fifteen minute intervals. Feed samples were taken directly from the feed stream exiting the feed tanks. Raffinate samples were taken from a sampling system which was equipped with a pressure let-down vessel to remove extraneous CO_2. Both feed and raffinate samples were collected in containers having covers with a septum so that they could be saved for post-run analysis on a gas chromatograph.

The totalized level of organics in the CO_2 feed, extract, and the stream leaving the top of the distillation column was recorded using an on-line hydrocarbon analyzer. This was extremely useful in achieving steady state for a given set of run conditions and for closing materials balances on the extractor for data analysis.

Pilot Plant Process Flow Diagram

The pilot-plant process flow was similar to that of a liquid-liquid extraction system. The hazardous aqueous waste feed was contacted with the CO_2 solvent in a counter-current sieve tray extraction column. The raffinate, stripped of organics, was discharged from the bottom of the extractor. The extract stream containing solvent and extracted organics was sent to a solvent stripping column. The solvent vapor was recovered from the top of the still, with the bottoms being substantially enriched in the organics product. The overhead vapor was compressed, then passed

through the tubeside of the reboiler. There, the vapor was condensed, giving up its latent heat to boil-up the shellside liquid. The condensed CO_2 on the tubeside was then recycled to the extractor.

Flowsheet

The pilot plant process flowsheet is shown in Figure 3. The primary operations are extraction, distillation, and vapor recompression.

Feed was prepared in two 35-gallon stirred stainless steel tanks. It was pumped from the tank to the extractor. The aqueous phase, which was the continuous phase, flowed from stage to stage through downcomers in the extractor. After passing through the extractor, the raffinate was flashed through a metering valve to atmospheric pressure, and the liquid was collected in a 35-gallon raffinate tank. The CO_2 vapor which flashed out of the liquid upon pressure reduction was vented.

The liquid CO_2 solvent bubbled up through the extractor, coalescing above the extractor's uppermost tray. The position of this aqueous-CO_2 interface is referred to as the "extractor interface" or the "upper extractor interface". A similar interface existed at the bottom of the extractor and between each set of sieve trays. This CO_2-rich phase exited via the extract line and was regulated by a back-pressure control loop maintaining a set extractor pressure.

The pressure drop of the extract stream through control valve, CV-1, was accompanied by a temperature drop and a partial flashing of liquid CO_2 to vapor. Since the solubility of water in CO_2 decreases with decreasing temperature, it was expected that in addition to CO_2-rich liquid and vapor phases a water-rich phase should form with the temperature drop and vapor formation. The decanter through which the extract passed before entering the still was intended to remove the H_2O-rich phase from the extract stream. In practice, the decanter also removed water which was inadvertently carried out of the extractor as entrained dense phase in the extract.

The CO_2-rich liquid-vapor mixture was drawn off the top of the decanter and sent to the still. Because of the high volatility of CO_2 relative to the organics product, the still's major function was to vaporize CO_2. A mixture of approximately 50 wt% CO_2 was maintained in the reboiler. The overhead vapor was at least 90% CO_2.

The reboiler bottoms was drawn off to maintain a constant liquid level in the reboiler. This stream was flashed to atmospheric pressure through CV-5 then into the product

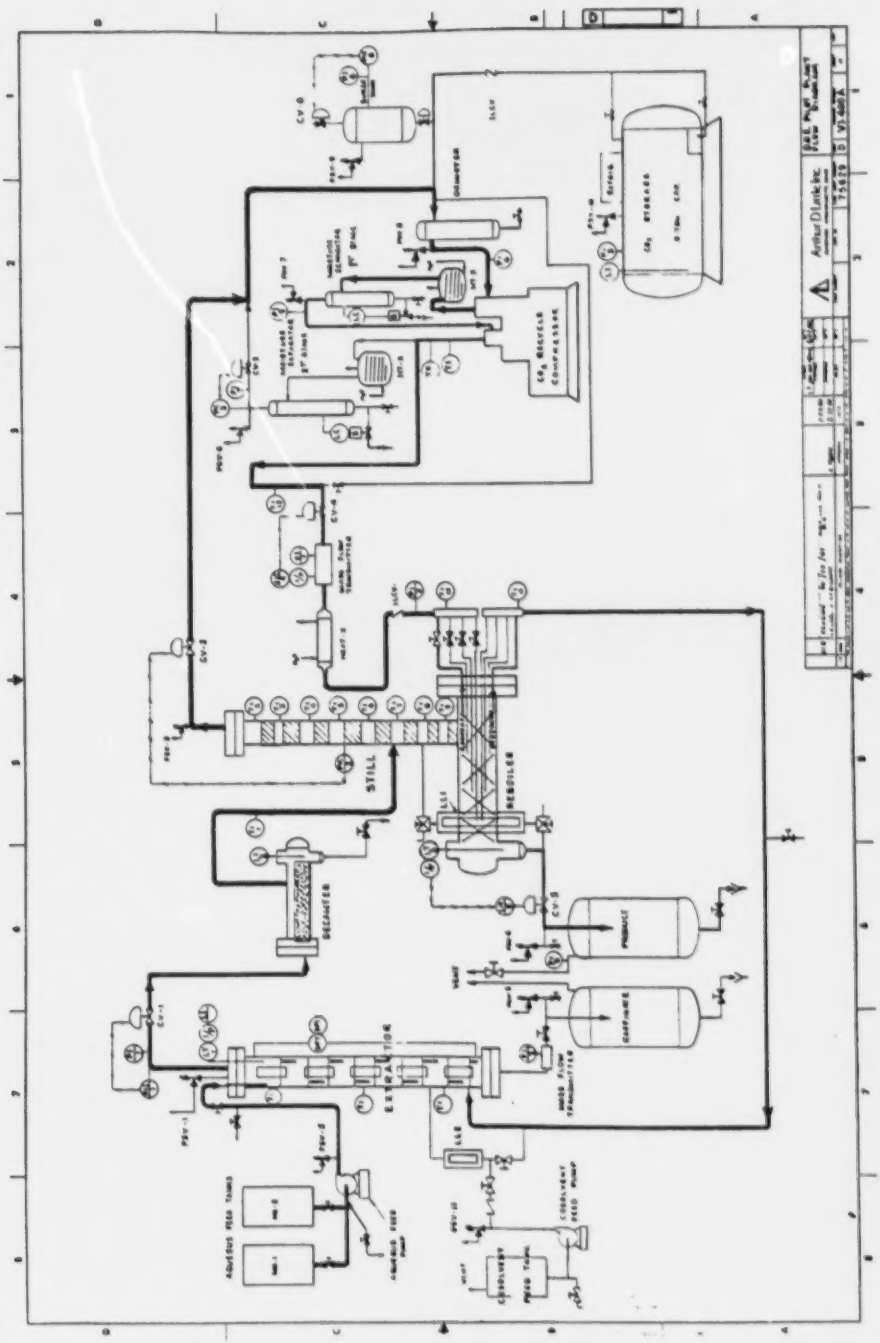


FIGURE 3 - PROCESS FLOW DIAGRAM OF SUPERCRITICAL LIQUID/LIQUID EXTRACTION PLANT

collection tank. The CO_2 vapor resulting from the flash was vented. There was no meter to measure the volume of CO_2 vented.

Vaporized CO_2 from the top of the still passed through back pressure control valve, CV-2, flashing to the compressor's inlet pressure.

The CO_2 vapor was combined with make-up CO_2 and recompressed. The vapor leaving the compressor was at a higher temperature and pressure than required for recycle to the reboiler. The outlet vapor passed through a flow control valve, where its pressure was reduced to extractor pressure. Excess heat was removed in the trim heat exchanger, then the hot vapor entered the reboiler. The vapor was condensed in the reboiler tubes; however, since the pressure was in excess of the critical pressure there was no actual phase change, although there was a large density change. The CO_2 was then recycled to the extractor as fresh solvent.

Since the design intent was to have the pilot plant operation both simple and flexible, one compressor was used for all pilot plant services. This included pressurization of CO_2 during start-up, pressurization of make-up CO_2 and CO_2 recycle, as well as operation at high flows and pressures. Thus, the inlet pressure for the compressor was 250 psi, and the exit pressure 1500 psi. This resulted in the necessity of reducing the still tops pressure.

While the oversized compressor allowed flexibility of operation, a by-pass control loop was required in order to maintain desired flowrates. The compressor was run at full capacity and the discharge stream was split. One portion was flashed through a back-pressure control valve to the compressor inlet. The remainder of the stream went to the process.

Carbon dioxide was stored in a 6-ton capacity tank at 300 psi and 32°F. Both vapor and liquid draw offs were available, with vapor supplied to the compressor inlet surge vessel.

Comparison with Commercial Scale Flowsheet

There were many minor differences between the pilot and commercial scales of operation; however, the one major variation was in the compression scheme. While a typical commercial design has three or more compressors, each operating at a different pressure, the pilot plant had only one compressor. This required the still tops to be flashed to low pressure before being recompressed. Also, the raffinate stream and reboiler bottoms were flashed directly to atmospheric pressure, with CO_2 gas vented

rather than recovered. The industrial process call for these streams to be flashed to intermediate pressures, heated and then flashed to atmospheric pressure, with the CO_2 vapor collected and recompressed. No heat was supplied to any flashing stream in the pilot plant. The pilot plant was also designed for use under a wide range of conditions and capacities, and it was instrumented for collection of design data.

The pilot plant extractor was much shorter and had fewer sieve stages than an industrial unit. Space, handling, and availability considerations all contributed to the decision to limit the pilot plant extractor height to approximately 7 ft. In most cases, this did not result in the high recovery which an industrial design demands. However, it was well suited for studying capacity and mass transfer efficiency.

Equipment List

The extractor specifications were as follows:

1. 4" diameter x 80" vertical vessel;
2. Design pressure: 2000 psi;
3. Design temperature: 150°F;
4. Stainless steel construction;
5. Interface level control;
6. Pressure control;
7. Removable sieve-tray stack consisting of 8 trays with 7 inch spacing;
8. Each tray had approximately 90 0.125" holes which were on a 2.5 diameter center-to-center spacing on a triangular pattern;
9. The downcomers were 1.125" diameter with removable orifices; this allowed the downcomer diameter to be reduced down to 0.25".
10. The tray stacks were a combination of teflon and stainless steel.
11. There were temperature, pressure, and liquid-liquid interface indicators for the extractor; in addition, each sieve tray could be viewed through the extractor windows and its performance observed.

The distillation column specifications were:

1. 4" diameter x 60" vertical vessel;
2. Design pressure: 1400 psi;
3. Design temperature: 150°F;
4. Stainless steel construction;
5. 8 sections, each 6" long, of wire-mesh packing;

6. Stripping section; rectifying section;
7. Indicators included still pressure and 5 thermocouples along the length of the still;
8. Pressure control;
9. The still was mounted directly on the reboiler;

The reboiler specifications were:

1. 6" diameter x 40" horizontal vessel;
2. Design pressure: 1400 psi shell side and 2000 psi tubeside;
3. Design temperature: 200°F;
4. Four heat-exchanger coils, each 0.5" stainless-steel tubing with a wall thickness of 0.065", and 10' long;
5. The coils were in parallel and each had its own shut off valve so that the active surface area within the heat exchanger could be varied for measurement of heat transfer characteristics;
6. Level was maintained in the reboiler by controlling the liquid bottoms product flow.

The compressor was a two-stage reciprocating, oil-free, carbon dioxide compressor:

1. 250 psi inlet pressure;
2. 700 psi interstage pressure;
3. 1500 psi discharge pressure;
4. Interstage and aftercoolers were water-cooled;
5. Capacity was about 20 lbs/min;
6. Discharge pressure was maintained with a back pressure bypass-to-suction control loop.

The decanter specifications were:

1. 4" diameter x 30" horizontal vessel;
2. Design pressure: 1400 psi;
3. Design temperature: 125°F;
4. Packing was a wire-mesh coalescer.

The feed-pump specifications were:

1. Maximum capacity: 100 gph, variable from 1-100% of capacity by adjusting stroke length;
2. Maximum discharge pressure: 2000 psi.

Plant Operating Procedures

Due to its flexible design, the pilot plant could be operated in a variety of ways. The operating procedure given here was one which was frequently used. It was only one of many operating procedures.

Start-Up

Several items of preparation were performed routinely. The thermocouple indicator was zeroed using an ice-water bath and a reference thermocouple. All tanks and vessels were pressurized to low pressures (10-20 psi) with air or CO_2, in order to blow out any trapped liquids.

The aqueous feed pump was turned on and set for the flowrate desired (2-5 lb/min.). When the extractor was roughly 3/5 full of aqueous solution, the CO_2 storage tank valve was opened, along with the CO_2 flow controller, to pressurize the system to 250-300 psi. At this time the raffinate and product flash control valves were both closed, as was the still-pressure control valve.

With the extractor 3/5 full and the pressure at 250 psi throughout the system, the cooling water to the compressor and the trim heat exchanger was turned on. The extractor and still pressure controllers were then set for the desired operating pressures. The raffinate control needle valve was opened slightly.

With the manual by-pass loop around the compressor fully open, the compressor was turned on.

With the extractor pressure control valve closed, the pressure in the extractor increased rapidly from 250 psi to the saturation pressure at the extractor temperature, usually between 850 and 1000 psi. Liquid CO_2 began to condense in the extractor and the extractor pressure remained constant until the extractor was full of liquid CO_2.

At this time the compressor manual by-pass control valve and the CO_2-solvent flow control valve were adjusted so that the approximate flow rate desired of CO_2 was flowing into the extractor. When the extractor was full of liquid, the pressure again rose rapidly until it reached the 1200-psi setpoint, and the pressure control valve opened, allowing extract to flow out of the extractor.

During this pressurization, the extractor interface level was observed, and the raffinate control valve adjusted. The proper setting matched the feed and raffinate flows, such that the extractor interface level was constant. This adjustment could be made by either observing the interface level in the extractor window or using the capacitance level indicator.

As CO_2 started to enter the still, the still pressure rose to the set pressure, between 600 and 750 psi. As this pressure was approached, the still-pressure control valve opened, and CO_2

started flowing from the still back to the compressor inlet. The sight gauge in the still tops line was observed, ensuring that the still was not flooded and that only CO_2 vapor was in the still tops.

With the extractor and still operating at the desired pressures, flowrate changes could be made. The raffinate control valve was adjusted to match any change in feedrate. While these adjustments were made the compressor inlet, interstage, and outlet temperatures and pressures, as well as the extractor temperature, were observed and adjusted as necessary.

Operation

Once the set flowrates and hydraulic balance in the extractor had been obtained, the extractor began to approach mass-transfer or compositional steady-state. The time required to reach this steady-state condition depended on both the feed and solvent flowrates. Steady-state was determined by continuous real time compositional analysis around the extractor by hydrocarbon analyzer. Generally, 1.5 to 2 aqueous hold-up volumes had to be displaced before the raffinate concentration stabilized.

In addition to monitoring organic levels with the hydrocarbon analyzer, both raffinate and feed samples were taken every fifteen minutes during an experimental run. These were labeled and saved for post run analysis on a gas chromatograph.

While running, the liquid levels of the feed tank, the raffinate receiver and the reboiler were checked frequently, and adjustments made as needed. Any aqueous phase which collected in the decanter was manually removed and sampled. In addition all of the data required for the run sheets was recorded which included the temperature and pressure readings and flow rates determinations.

Shut-Down

The system was quite simple to shut down. The feed pump and the raffinate control valve as well as a valve in the feed line were shut off simultaneously. The CO_2 tank valve was closed. The flow of CO_2 through the extractor was reduced by partially closing the flow control valve and opening the manual by-pass valve. The power to the compressor was then turned off. When the compressor was turned off, to avoid a high pressure surge to the compressor inlet, which in turn activates a relief valve, the surge vessel pressure control valve was manually opened at the same time that compressor power was shut off. CO_2 in the system was also vented via the product flash vessel. After the raffinate tank had been drained, the residual aqueous solution in the extractor was drained. All raffinate and extractor samples and residues were weighed to complete the mass balance.

SECTION 4

FEED SPECIFIC EXPERIMENTAL APPARATUS AND OPERATING PROCEDURES

STEEL MILL SLUDGE WASTE

Feed Related Modifications of Apparatus

The liquid-liquid extraction unit was used for experiments using the steel mill sludge as feedstock. The nature of the feed required several changes to the system and still caused a great deal of trouble in system operation. The primary problem is that the system was intended for liquid-liquid extraction of a particulate-free feed stream. The sludge had a particulate loading of two to five percent by weight.

The first change made was in the configuration of the downcomers. The restriction plugs usually used were replaced with blank disks of teflon and the downcomer sides were drilled to allow flow out of the side of the tube. This is shown in figure 4. The desired effect was to break up the flow of the aqueous stream to prevent the particulates from piling up on the tray below the downcomer. An additional effect was to decrease the chance of solvent phase bypass which would occur if the solvent bubbles entered the bottom of the downcomer.

Operation of the facility highlighted other problems. The first difficulty encountered was with the level control loop used to maintain the level of the primary interface. This loop has a capacitance type level probe. Steel-containing sludge agglomerated on the probe and gave a false signal to the control loop. It was determined that the level would require manual control.

The second problem quickly presented itself. The valve controlling raffinate flow leaving the extractor became fouled by the entrained particulates in the liquid stream. The orifice of the control valve had a diameter of only 0.0012 inches since it was sized to control a two pound per minute flow at a 1000 psi pressure drop. This orifice was correct for a clear liquid but was easily fouled. Other manual control valves were tried, but all would plug when the flow was throttled to the operating flowrate. The erosion of the valve stem and seats was also a difficult problem. One stainless steel needle valve was completely destroyed in two hours of operation.

The solution to getting the raffinate (and the entrained steel particulates) out of the exractor was partially solved by setting up a lock-hopper arrangement made from 1/2" stainless steel tube with electrically actuated ball valves at either end. These valves were set on a timer to allow for the filling, and then the emptying of the tube. At the maximum cycle time of the valves the

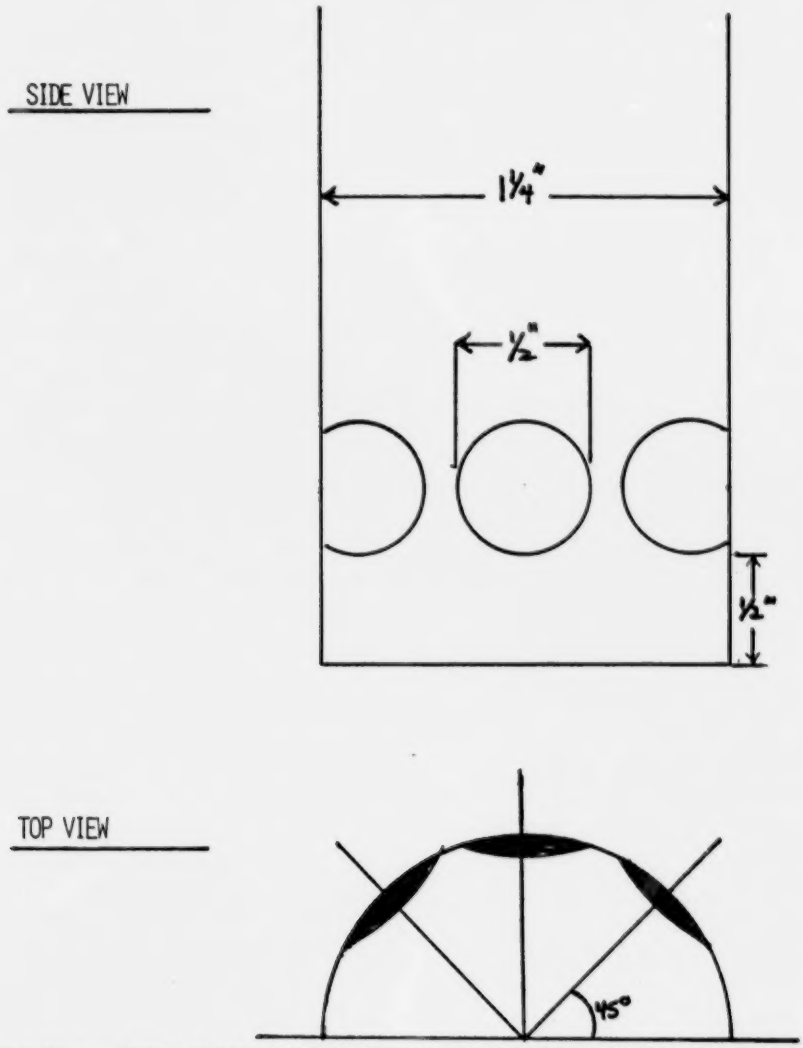


FIGURE 4. MODIFICATION OF DOWNCOMER DESIGN FOR STEEL MILL SLUDGE WASTE EXTRACTION

lock-hopper could accommodate a flow of about one pound per minute. This then became the maximum feed flowrate. The lock-hopper configuration was not the ultimate solution; the ball valves had a life expectancy of about three hours, at which time the downstream seat of both valves would be pitted beyond usefulness.

Operating Procedures

The extraction experiment was carried out by first filling the extractor half full of clean water. The solvent would then be admitted to the vessel and the compressor turned on to bring the system up to operating pressure. When the carbon dioxide flow path was stable, clear water was then fed to establish the flowrate. When the system was operating at hydraulic steady state the feed tank valves would be switched over to send the sludge into the extractor. Feed and raffinate samples were then taken after allowing a 30 minute period to re-establish hydraulic steady state.

Samples were analyzed for oil content by performing a Soxhlet extraction using Freon-113 on oven-dried residues. A sample for oil analysis was dried overnight in an oven at 100 C. An aliquot of the dried material was then weighed and extracted in a Soxhlet extractor overnight. The solvent was then evaporated from the flask and the residue weight determined. This residue in the flask was taken as the oil content of the original sample. Oil contents are reported in Section 5 on a dry basis.

PESTICIDE WASTE

Preparation of Feed

The feed was prepared by reformulating an actual waste stream. The pesticide manufacturer shipped the bottoms or sludge portion of the waste slurry described in Section 1. The slurried waste was composed of the following components with proportions given in weight percent:

Mixed xylenes	5%
Carbon tetrachloride	1%
Bottoms sludge	5%
Water	89%

The waste stream represents the pre-decantation slurry. Experimentation presented here represents an attempt to extract both xylene and carbon tetrachloride from the slurry before the decanting process.

Mixing in the feed tanks was maintained throughout all runs to homogenize this feed. Incomplete mixing would allow the waste to settle into a multiphase feed thereby complicating data analysis later.

Operating Procedures

The operating procedures and equipment used for this feed were the same as those listed in Section 3. for both laboratory and pilot plant scale extractions.

Experimental Outline

Laboratory scale experiments were run first to study the feasibility of extracting xylene and carbon tetrachloride with carbon dioxide from this feed. Distribution coefficients were determined from which a suitable range of solvent-to-feed ratios could be chosen for pilot plant scale extractions.

Two pilot plant experiments were run. First, two different solvent-to-feed ratios were used (2 to 1 and 1 to 1) to examine the effect of the relative amount of solvent on extraction. Second, a multipass experiment was run where the raffinate of a previous pass (ex. raffinate from pass #1) was used as the feed for the next extraction pass (ex. feed for pass #2). This was done to simulate a taller extraction column. A solvent-to-feed ratio of 1 to 1 and a reflux ratio of 1 to 1 were used for the multipass experiment.

Raffinate and feed samples were taken, and these were analyzed for every fifteen minutes during the runs on the gas chromatograph for xylene and carbon tetrachloride levels. Only the aqueous portion of the multiphase feed and raffinate samples were tested. Concentrations of these components were determined by comparing gas chromatogram areas from standards of known concentrations with areas from samples of feed and raffinate.

DISSOLVED ORGANICS WASTE

Preparation of Feed

The feed was prepared by reformulating an actual waste stream. The synthetic feed was based on an actual waste stream of an acrylonitrile manufacturing plant described as the predominantly dissolved organics waste stream in Section 1. The waste was

composed of the following components with proportions given on a weight basis.

Ammonium sulfate	2.0%
Acetonitrile	350 ppm
Acrylonitrile	250 ppm
Water	97.9%

This waste stream represents a diluted waste stream in the overall acrylonitrile manufacturing process. The conceptual design section of this report, based on this process, will handle an extraction before a 4.8 to 1 dilution takes place with water. The dilution was done to allow disposal by deep-well injection.

Operating Procedures

The operating procedures and equipment used for this feed was the same as those listed in Section 3 for both laboratory and pilot plant scale extractions.

Experimental Outline

Laboratory scale experiments were first run to study the feasibility of extracting acetonitrile and acrylonitrile with carbon dioxide from this feed. Distribution coefficients were determined from which a suitable value of a solvent-to-feed ratio could be chosen for pilot plant scale extractions.

Experimentation based on laboratory scale extraction results was limited to a multipass experiment using a solvent-to-feed ratio of 1.5 to 1 and a reflux ratio of 1 to 1.

Raffinate and feed samples were taken every fifteen minutes during experimentation. These were analyzed on the gas chromatograph for acetonitrile and acrylonitrile levels. Concentrations of these components were determined by comparing gas chromatograph responses of run samples to those of standards of known concentration.

SECTION 5

RESULTS

STEEL MILL SLUDGE WASTE

Qualitatively the extraction of oil from the steel mill sludge with carbon dioxide was effective. The feed was a black particulate laden watery liquid that would not settle. The raffinate in all cases settled very quickly (within 15 seconds after shaking) and left a clear water phase above a black particulate layer. The raffinate was easy to filter and handle.

Pilot Plant Data

Results from the extraction of oil from the steel mill sludge waste are shown in Table 2.

Analysis of Results

The quantitative analysis of the extractions was less easy to explain. With the exception of the first run the extraction efficiencies follow solvent-to-feed ratio. There was not enough data to predict an optimum solvent-to-feed ratio for this extraction, but it is clear that a commercial process would operate above a solvent-to-feed ratio of 4 to 1. The increase in oil removal efficiency resulting from doubling the solvent-to-feed ratio does not warrant the increase in plant/equipment size or decrease in overall plant capacity that would ensue.

The dramatic results of the first run can be ascribed to a clean system. The sieve trays in the extractor were of a perforated plate design with 1/8" holes. A slight burr on the

TABLE 2. OIL EXTRACTION FROM STEEL MILL SLUDGE WITH CARBON DIOXIDE

Run	Dilution	Solvent-to Feed Ratio	Oil Content* Feed	Raffinate	Oil† Reduction
1	0	1.6	20.3%	10.9%	51.8%
2	1	4.6	19.5%	14.6%	29.4%
3	4	9.6	18.3%	13.2%	32.0%
4	4	2.0	18.3%	17.2%	7.1%

* Oil content in weight percent dry basis
† Oil reduction defined as (oil in feed - oil in raffinate) / oil in feed

upper side of the holes helps bubble formation, but also acted in this situation as a collection point for particulate solids. The trays each caught and held a layer of solids, and as the experiments progressed the holes in the sieve trays became blocked. This in turn dropped the number of theoretical trays in the extractor and consequently, lowered the overall performance of the system.

It was also difficult to interpret the effect of dilution on the extractor performance. The reason for dilution was solely to prevent valve blockage, but was found to be only moderately successful. A commercial plant would not be designed to use diluted feed.

Full Scale Plant Design Considerations

Our extraction experiments did not yield sufficient data to design a full scale sludge treatment facility, but do suggest that critical fluid extraction technology can be applied to the sludge problem. Several design modifications to a CFS process would result in a working plant. These design changes would revolve primarily around the particulate nature of the feed. A stirred tank (or mix-settler tank or series thereof) would replace the sieve tray extractor used for these experiments. Pumps would have to be able to handle the very abrasive slurry. Ceramic plunger positive displacement pumps with flushed packing may be the most suitable to reach the delivery pressures necessary and have a reasonable useful lifetime.

Control valves handling the raffinate stream would be a possible problem area. The plugging problems encountered in the pilot scale experiments would not be encountered in a full scale plant since the particulate size would stay constant and the control valve orifice size would increase to handle the higher flowrates of the commercial duty plant. Erosion of the control valve surfaces could be a serious problem, but the recent advent of ceramic ball valves used for control purposes may provide a solution to this problem.

PESTICIDE WASTE STREAM

Laboratory Data

Distribution coefficients were determined for the feed. This was done to investigate both ease of extraction with CO_2 and an appropriate range of solvent-to-feed ratios for pilot plant runs. The general procedure for laboratory scale extraction was followed, see Section 3.

The values of distribution coefficients obtained from the

bench scale system are listed here:

CARBON TETRACHLORIDE

	Feed Concentration	Distribution Coefficient
1	1380 ppm	12.9
2	1690 ppm	29.5

XYLENE

	Feed Concentration	Distribution Coefficient
1	1560 ppm	20.2
2	2350 ppm	70.7

The data indicated that the extraction of both xylene and carbon tetrachloride would be very easy with carbon dioxide as the solvent.

The feed contained three liquid phases and a solids phase at the bottom. Separation into three liquid phases was to be expected due to the density differences between carbon tetrachloride (1.59), water (1.0) and xylene (0.88) and to the solubility limits in water of carbon tetrachloride (800 ppm) and mixed xylenes (570 ppm).

In light of the solubility limits in water, the gas chromatography determinations of feed concentrations might present a contradiction. One would expect the aqueous portion of the feed to contain carbon tetrachloride and xylene at or near their solubility limit. This is not the case as one can see that the levels are on the order of 1000 ppm higher. The reason for this is due to the addition of soaps or dispersants by the manufacturer to the pesticide production process. This did not affect extraction results in the bench scale runs probably due to the high shear mixing of the feed with the solvent. However, as we shall see in the pilot plant runs these soaps may have severely hampered the extraction of the organics from the waste stream.

Pilot Plant Data

The results for the pilot plant runs are given in Tables 3 and 4 for the extraction of carbon tetrachloride and xylene, respectively. EPA Run #7 was used as both a solvent-to-feed ratio experiment and as the first of four passes of the multipass experiment.

TABLE 3. MULTIPASS EXTRACTION OF PESTICIDE WASTE
CARBON TETRACHLORIDE CONCENTRATION HISTORY

EXPERIMENT AND PASS NUMBER	TIME (MIN)	SOLVENT RATE LB/MIN	FEED RATE LB/MIN	FEED (PPM)	RAFFINATE (PPM)	% REDUCTION $(1-X_r/X_f)$
EPA 7/#1A	5	2.1	1.1	423	---	41.3
	10			386	284	
	20			583	230	
	35			488	237	
	45			446	280	
	60			502	380	
EPA 7/#1B	75	2.2	1.9	507	409	7.8
	85			473	454	
	95			407	454	
	105			558	---	
	115			599	515	
EPA 8/#2	125	4.7	4.1	394	284	
	130			460	207	
	140			390	ND	
	145			363	ND	
	150			384	ND	66.3
EPA 9/#3	160	4.7	4.3	199	191	
	170			230	193	
	175			220	174	
	180			124	182	4.3
EPA 9/#4	200	4.9	4.5	76	207	
	205			ND	ND	
	210			ND	---	
	215			ND	ND	
	220			ND	91	

TABLE 4. MULTIPASS EXTRACTION OF PESTICIDE WASTE
MIXED XYLENES CONCENTRATIONS HISTORY

EXPERIMENT AND PASS NUMBER	TIME (MIN)	SOLVENT RATE LB/MIN	FEED RATE LB/MIN	FEED (PPM)	RAFFINATE (PPM)	% REDUCTION $(1-X_r/X_f)$
EPA 7/#1	5	2.1	1.1	390	---	
	10			315	633	
	20			590	748	
	35			401	644	
	45			333	415	
	60			325	467	
EPA 7/#1	75	2.2	1.9	403	368	
	85			412	418	
	95			279	397	
	105			550	---	
	115			371	407	
EPA 8/#2	125	4.7	4.1	667	425	
	130			816	261	
	140			662	371	
	145			720	265	
	150			680	494	48.8
EPA 9/#3	160	4.7	4.3	528	889	
	170			615	879	
	175			607	757	
	180			395	850	
EPA 9/#4	200	4.9	4.5	285	1127	
	205			293	---	
	210			306	1199	
	215			222	968	
	220			244	900	

Gas chromatography was used to determine the organics levels in the aqueous portion of the feed and raffinate samples. The extremely small size of the possible two other liquid layers coupled by the presence of a high solids content therein would have precluded the use of gas chromatography to analyze these phases accurately. Thus, only the reduction of organics in the aqueous portion of the stream was analyzed.

It should be noted here that interest exists in treating the aqueous phase of the original waste separately to remove the carbon tetrachloride. A biotreatment plant used to treat this waste can only handle very low levels of chlorinated hydrocarbons as these are lethal to the bacteria used in the process.

Analyzing the aqueous phase in the presence of other phases would mean that the aqueous phase should contain the predominant organic of the additional phase at its equilibrium level (i.e. the solubility limit). This may be complicated by the presence of the soaps or dispersants.

Once again, solids were present throughout the feed, suspended in the aqueous, settled on the bottom and floating in the light portions of the samples. The same was true of the raffinate. However, the amount of solids in the aqueous portion of the raffinate was visually higher than in the feed. These samples were allowed to sit for two weeks, and while the aqueous portion of the feed became nearly clear, the raffinate remained cloudy indicating the presence of suspended solids.

Analysis of Results

The purpose of experimentation again was two-fold. The first was to examine the extractability of carbon tetrachloride, as carbon tetrachloride is extremely hazardous and also toxic to biotreatment plant bacterial cultures. The second was to recover the xylene in the waste which, as a recyclable solvent, would present significant economic gains.

Carbon Tetrachloride Extraction

EPA 7 Run #1A used a solvent to feed ratio of 2 to 1 and achieved a 41.3% reduction in one pass. While in Run #1B, a ratio of 1 to 1 was used and only 7.8% reduction was encountered. This indicates that in the extraction of carbon tetrachloride from water that an increased solvent to feed ratio is preferred except where economic constraints prevail.

The overall success of this multipass extraction experiment (EPA Runs 7, 8 and 9) can be looked at by an overall reduction of carbon tetrachloride. The extraction of carbon tetrachloride was very successful with an overall reduction of 79% in the aqueous portion. The overall % reduction was taken as the reduction from the average feed concentration in EPA 7 pass #1 to the final raffinate concentration in EPA 9 pass #4. This figure is presumably low for two reasons. The first raffinate sample from EPA 9 pass #4 is probably high due to carryover from pass #3. Recalculating the % reduction without this sample, the reduction comes to 86% overall. The below-minimum detection limit determined of 60 ppm is high and perhaps other methods of detection would show significantly greater reduction. Regardless, 60 ppm is used as the maximum minimum level achieved.

An experimental anomaly occurred during EPA Run #8 and potentially into EPA Run #9 in the raffinate levels of carbon tetrachloride. It should be noted here that starting with EPA Run #8 a solvent to feed ratio of 1 to 1 was used but that both flow rates were more than doubled. This was done to enhance turbulent mixing in the extractor of the multiphase feed. It was hoped that the increased mixing would simulate conditions in the stirred extractor used for the bench-scale extractions which enjoyed such great success. It is inexplicable, however, why the increased mixing would give such great results in pass #2 and #4 and literally no extraction whatsoever in pass #3.

Xylene Extraction

The results for the extraction of xylene are difficult to interpret. The discernible existence of a light phase in the raffinate in some samples indicated that the level of xylenes in the aqueous phase should be at least 570 ppm (the solubility limit of mixed xylenes in water).

No conclusions can be drawn on the effect of solvent to feed ratio on the extraction of xylene in EPA Run #7. The multipass experiment, however, indicated that not only was the xylene not being extracted from the aqueous phase but that its concentration was effectively doubled in the raffinate by pass #4 of Run #7. Even though this is essentially double the solubility limit, it could be explained that the soaps or dispersants permit this much xylene to be suspended in the raffinate.

A more likely explanation is in the process and not in the performance of the extractor. In the multipass experiments, the raffinate of a previous run was used as feed for the next pass. Feed was sampled directly from the feed tanks while the raffinate was sampled from a system of lines which could potentially entrap

xylene. The raffinate of EPA Run #9 pass #3 with an average of 845 ppm of xylene was the same body of material used as EPA Run #9 pass #4's feed with an average of 270 ppm of xylene. Taking the feed from pass #4 as the raffinate from pass #3, a 60% reduction in xylene was achieved overall in just two passes (pass #2 and pass #3).

Full Scale Plant Design Consideration

It is suggested here that future work on this waste stream concentrate on this single aqueous phase. Significant reductions in the carbon tetrachloride level are achievable. This could present a great benefit to manufacturers who treat pesticide wastes in biotreatment facilities, since chlorinated hydrocarbons are harmful to their bacterial cultures.

Interpretation of the data from the extraction of xylene was difficult due to an anomaly between feed and raffinate samples. There was, however, an apparent reduction of xylene in the multipass experiment. This reduction may or may not present significant economic advantages with its recovery. Most certainly, a review of the raffinate sampling system is in order to see if entrapment of low density liquids can occur in this system, which would affect raffinate concentration analysis.

Finally, given the extreme success of extraction in the laboratory scale stirred extraction, a full scale plant design should be based on a stirred tank or mix-settler type extractor. This would also circumvent the problems encountered when operating with high amounts of solids present in the feed.

DISSOLVED ORGANICS WASTE

Laboratory Data

The distribution coefficient data for the dissolved organics waste stream indicated that the extraction of acrylonitrile would be very easy with CO_2 and that acetonitrile would be the limiting component, but not a difficult extraction either. A solvent-to-feed ratio of 1.5 to 1.0 was chosen based on this data for the pilot plant experimentation.

ACETONITRILE

	FEED CONCENTRATION	DISTRIBUTION COEFFICIENT
1.	2100 PPM	0.9
2.	1750 PPM	0.6

ACRYLONITRILE

1.	1650 PPM	5.5
2.	997 PPM	4.5

As was indicated by the name "Dissolved Organics Waste", both the feed and raffinate were single phase and clear. All the ammonium sulfates easily went into solution and were not expected to interfere with extraction. Further design work on this process must, however, investigate the possibility of ammonium sulfates consuming the solvent carbon dioxide through the production of bisulphite ions. The chemical equilibrium of conditions and chemical species present during extraction must be looked at more closely to truly describe solvent requirements for a conceptual design.

Pilot Plant Data

A multipass extraction was conducted for this feed with a solvent-to-feed ratio of 1.5 to 1.0 and a reflux ratio of 1 to 1. The raffinate from a previous pass was used as the feed for the next pass as in the pesticide run. The running of the experiment was uneventful due to the absence of solids or multiple phases in the feed. The results of the extraction were so good that this feed was chosen as the basis of a conceptual design which is presented in Section 6 of this report.

The analysis of the feed and raffinate samples done on the gas chromatograph gave a high degree of repeatability both within samples and between samples for a given pass as seen in Tables 5 and 6. This was an indication that indeed the feed for each pass was homogeneous.

As predicted by the distribution coefficient data, acrylonitrile extracted much more easily than the acetonitrile. In just one pass through the extractor, 99% of the acrylonitrile was recovered while three passes were required to recover the same percentage of acetonitrile.

Tables 5 and 6 list the concentrations of acetonitrile and acrylonitrile in the feed and raffinate throughout the multipass experiment. Also listed is the percent recovered of the organic per pass through the extractor. Recovery here was defined as $(X_f-X_r)/X_f$ or more simply as $1-(X_r/X_f)$. One can see that as the feed concentration dropped, the driving force for mass transfer was lowered and recovery percentages dropped off as well. Figures 5 and 6 depict the compositional history of acetonitrile and acrylonitrile during the multipass experiment. These graphs demonstrate the dramatic drop off in solute level after the first pass.

The non-detectable limit of one part per million was less than or equal to two times the average noise level of the gas chromatograph. The minimum detection limit was taken as when the error of precision was greater than or equal to 25%, which is given as:

$$\text{Error of Precision} = \frac{X_i - X}{X} \times 100$$

X_i = Individual reading
X = Mean

Thus, when a standard of known concentration at 2 ppm was injected, the error of precision incurred was greater than 25%.

Even though the feed for each pass was the raffinate of the previous pass, organics levels in the two streams were different. The higher concentration present in the feed was probably due to residual organics present in the system between the feed and raffinate tanks.

The extractor analysis presented in this next section was based on this feed. The analysis of the extractor's performance for the pesticide and steel mill sludge wastes was not performed due to the non-homogeneity of the feed. When multiple liquid phases and solids are present, a McCabe Thiele analysis cannot be effective. The extractor efficiency calculated was based on the extraction of the acetonitrile component. This was done because the acetonitrile, based on both laboratory and pilot plant data, was more difficult to extract. A commercial scale extractor was then designed based upon an efficiency calculated in this next section.

TABLE 5. MULTIPASS EXTRACTION WITH DISSOLVED ORGANICS WASTE; ACETONITRILE CONCENTRATION HISTORY

PASS NUMBER	TIME (min)	FEED (ppm)	RAFFINATE (ppm)	RECOVERY $(1-X_r/X_f)$ %
1	5	----	26	89
	15	342	27	
	30	370	38	
	40	368	50	
	50	340	39	
2	65	---	21	75
	85	43	12	
	95	43	10	
	100	45	---	
	105	---	11	
3	120	17	5.1	81
	130	18	3.9	
	140	19	3.4	
	145	18	3.1	
	160	---	3.8	
4	165	5.8	---	69
	170	---	2.1	
	175	6.2	---	
	180	---	BMDL*	
	185	5.7	---	
	190	---	BMDL	
	195	8.1	2.3	
5	245	---	BMDL	---
	250	---	BMDL	

*BMDL: Below Minimum Detection Limit (2 ppm)

TABLE 6. MULTIPASS EXTRACTION WITH DISSOLVED ORGANICS WASTE; ACRYLONITRILE CONCENTRATION HISTORY

PASS NUMBER	TIME (min)	FEED (ppm)	RAFFINATE (ppm)	RECOVERY $(1-X_r/X_f)$ %
1	5	---	2.0	99
	15	267	2.6	
	30	292	2.7	
	40	288	3.3	
	50	261	2.4	
2	65	---	BMDL*	77
	85	9.0	BMDL	
	95	8.5	BMDL	
	100	8.8	---	
	105	---	BMDL	
3	120	2.3	ND†	64
	130	3.2	ND	
	140	2.8	ND	
	145	2.7	ND	
4	160	---	ND	---
	165	ND	---	
	170	---	ND	
	175	ND	---	
	180	---	ND	
	185	ND	---	
	190	---	ND	
	195	ND	ND	
5	245	---	ND	---
	250	---	ND	

*BMDL: Below Minimum Detection Limit (2 ppm)
†ND: Not Detected (less than 1 ppm)

FIGURE 5

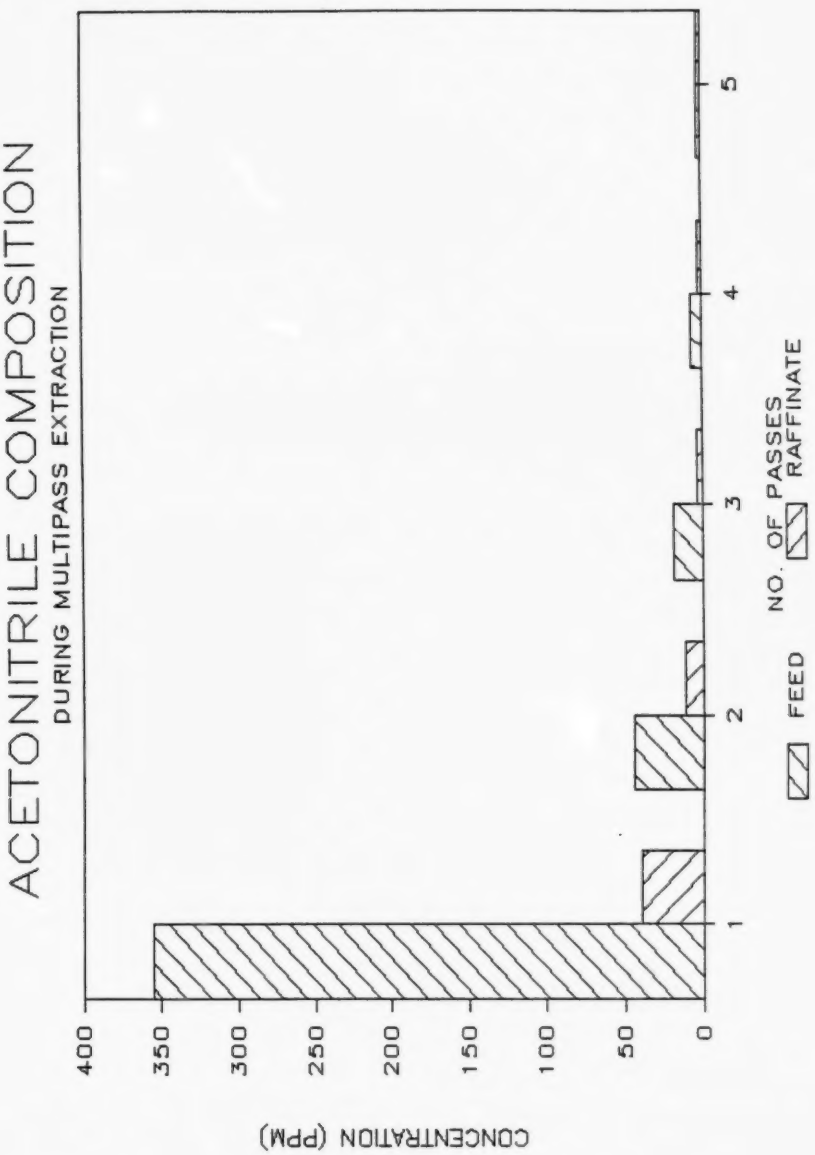
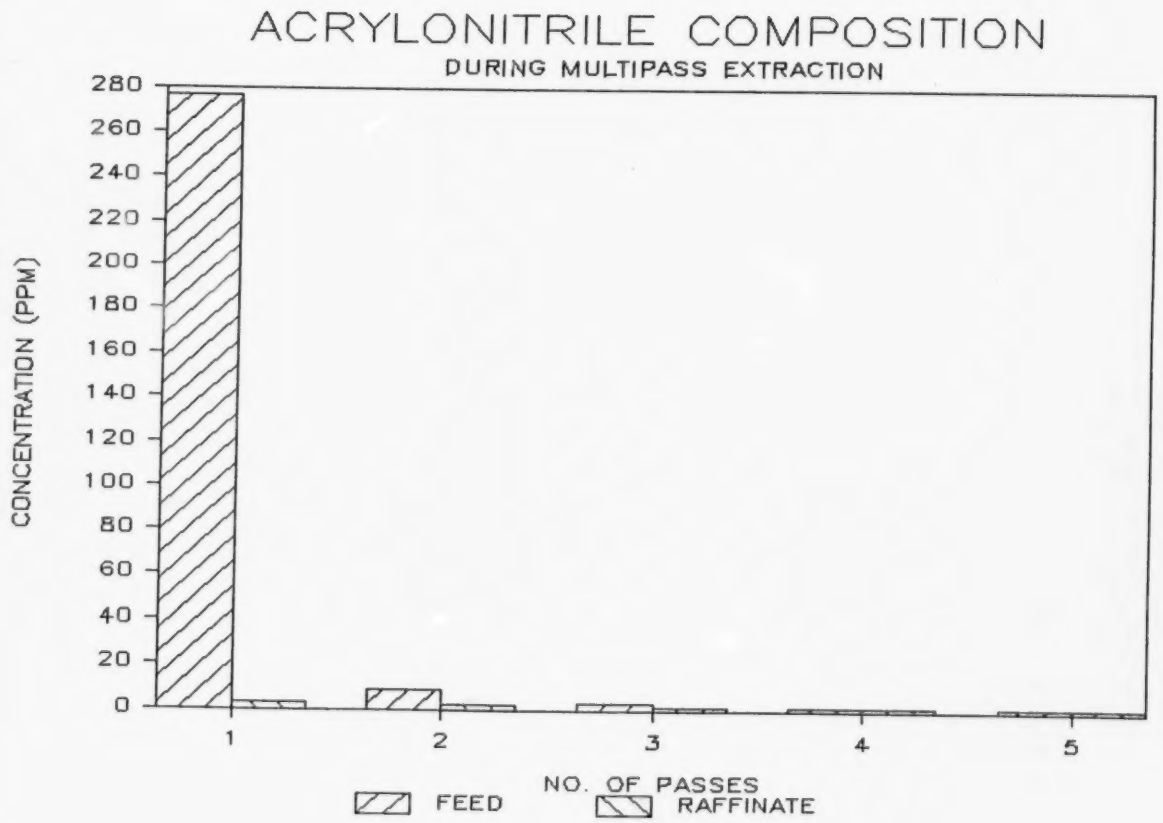

ACETONITRILE COMPOSITION
DURING MULTIPASS EXTRACTION
CONCENTRATION (PPM)
400
350
300
250
200
150
100
50
0
1
2
3
4
5
NO. OF PASSES
FEED
RAFFINATE

FIGURE 6


ACRYLONITRILE COMPOSITION
DURING MULTIPASS EXTRACTION
CONCENTRATION (PPM)
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
1
2
3
4
5
NO. OF PASSES
FEED
RAFFINATE

Analysis of Results

Material Balance

A material balance was calculated for each pass of the multipass experiment. The material balance was based on the total amount of acetonitrile and acrylonitrile present in the four streams monitored around the extractor. Feed and raffinate concentrations were measured by gas chromatography, while extract and solvent stream concentrations were measured by an on-line hydrocarbon analyzer.

The overall material balance was a gauge of the quality of concentration measurements. If a material balance closed then this was a good indication that all materials were accounted for. The amount of carbon dioxide used was measured using a flowmeter so that concentrations in the extract and solvent streams could be calculated on the same weight basis as the other two streams.

Table 7 lists the material balance calculations on a mole fraction in water basis for the four passes. Material balance closure-1 (MBC (1)) gives the relative percent error of the balance, and MBC(2) gives the absolute error in parts per million.

The results of this analysis indicate that once low levels of organics had been achieved, the error in measurement became magnified. An absolute error in the first pass of 34 ppm only resulted in a 5% deviation from a perfect material balance closures. Whereas, a 6 ppm error in the fourth pass resulted in a 43% deviation from a perfect material balance closure. An obvious source of error was the use of two methods for determining stream concentrations. There is, or course, an error associated with each method which becomes additive.

The values for feed and raffinate concentrations were averaged within a pass and averaged for a given sample. The error incurred here was due to sampling and to gas chromatograph analysis which could be attributed to injection technique or to the gas chromatograph itself.

The error attributed to the hydrocarbon analyzer readings may have a number of sources as well. Carbon dioxide streams readings were converted to a water basis by using an averaged solvent-to-feed ratio value which fluctuated throughout experimentation. This fluctuation would have a more significant effect on low level readings for the extract concentrations. Also, only a 570 ppm organics standard gas was available to calibrate the hydrocarbon analyzer. The further readings are registered away from this known data point, the more suspect they are of error. It

was concluded that if any analysis below the 12 ppm level is to take place a much greater degree of accuracy and precision must be present to have any confidence in the analysis.

Equilibrium, Mass Transfer Rates and Efficiency

The extractor's performance was analyzed for the dissolved organics waste feed described in Section 1 of this report. Acetonitrile was chosen as the solute of primary interest for the analysis over acrylonitrile due to its being relatively more difficult to extract. This assumption was based on the experimentally determined distribution coefficients of acetonitrile and acrylonitrile which were approximately 0.76 and 4.5, respectively.

TABLE 7. COMPONENT MATERIAL BALANCE AROUND EXTRACTOR FOR MULTIPASS EXTRACTION WITH DISSOLVED ORGANICS WASTE

PASS	FEED CONC. (ppm)	RAFFINATE CONC. (ppm)	EXTRACT* CONC. (ppm)	CO_2 IN (ppm)	MBC(1) (%)†	MBC(2) (ppm)**
1	640	43	633	2	95	34
2	52	13	65	2	69	24
3	21	3	38	2	56	18
4	6	2	12	2	57	6

*Extract readings have been converted to aqueous equivalents (i.e., multiplied by 1.5).

†Material Balance Closure (1) = organics in divided by organics out x100

**Material Balance Closure (2) = organics out - organics in

The acetonitrile-water-CO_2 equilibrium data, combined with the material balance and compositional analyses of the four streams entering and leaving the extractor, gave the information required to perform an extractor analysis. The McCabe-Thiele graphical method or the Kremser-Brown-Souder analytical method can be used to analyze the extractor's performance for a given set of conditions. A number of theoretical plates were calculated using the Kremser equation which gave the efficiency of the actual sieve trays.

The information needed to perform the analysis included the equilibrium data given by the experimentally determined distribution coefficients, and the following four terms:

(1)	Solvent-to-feed ratio	(S/F)
(2)	Feed composition	(X_f)
(3)	Raffinate composition	(X_r)
(4)	Solvent composition	(Y_s)

The S/F, X_f, and X_r were measured with a high degree of confidence. Y_s was measured with a total hydrocarbon analyzer which was taken to the total amount of acetonitrile and acrylonitrile present in the recycled CO_2 stream.

These four parameters were used to determine the number of theoretical trays necessary for the extraction in each pass. The tray efficiency was then calculated for each pass using the equation given below:

$$E = \frac{N \text{ (theoretical)}}{N \text{ (actual)}}$$

This efficiency was then used to design an extractor for an actual plant where the effect of purity of raffinate and solvent-to-feed ratio on sizing the extractor were investigated.

A constant distribution coefficient was used in the extractor analysis. The use of a linear equilibrium line allowed for the use of the Kremser equation given below:

$$N_{th} = \frac{\text{LOG}\left[\dfrac{(X_f - Y_s/m)}{(X_r - Y_s/m)}\left(1 - \frac{1}{Q}\right) + \frac{1}{Q}\right]}{\text{LOG } Q}$$

where m = distribution coefficient
N_{th} = number of theoretical trays
Q = S/F x m

Results

Analysis 1:

The first analysis of the pilot plant data for the multipass run on the dissolved organics waste feed is given in Table 8. The basis for this analysis was that the distribution coefficient was constant and taken as an average of the two points determined in the laboratory. The extractor analysis was based on the acetonitrile-water-CO_2 equilibrium system. Here, Y_s, the concentration of acetonitrile in the feed, was taken as the same as the total hydrocarbon reading given by the hydrocarbon analyzer. The Kremser equation was used to determine the number of theoretical trays for each pass and an extractor efficiency was calculated for each pass. The N_{th} was indeterminate for the last pass as Y_s/m exceeded X_r. This led one to believe that either Y_s, X_r or m were not accurate. The numbers of Y_s and m are more suspect of error than Y_r. An average tray efficiency (E) of 0.55 for the four passes was calculated.

Analysis 2:

The vapor pressures of acetonitrile and acrylonitrile were determined in the distillation column to determine the relative concentrations of these organics in the recycled CO_2 which originates here. The Clausius-Clapeyron equations for the two organics were determined from temperature, vapor pressure data given in the literature[5,6]. Given the still conditions of 56°F and 38,260 mm hg, partial pressures for acetonitrile and acrylonitrile were 52.7 mm and 65.5 mm, respectively. From these relative weight fractions for the two were determined from the total hydrocarbon analyzer reading. For analysis 2, Y_s is taken to be 8×10^{-7} as opposed to the total reading of 1.7×10^{-6} used in analysis 1. The results from analysis 2 are shown in Table 8.

Acetonitrile

$$\text{LOG } P(\text{mm}) = 1.7 \times 10^3 \, (1/T^{\circ}K) + 7.78$$

Acrylonitrile

$$\text{LOG } P(\text{mm}) = 1.8 \times 10^3 \, (1/T^{\circ}K) + 8.00$$

P = pressure in millimeters mercury
T = temperature in degrees Kelvin

Employing the new Y_s, a tray efficiency (E) of 0.43 was determined which indicated that the actual number of plates

TABLE 8. EXTRACTOR EFFICIENCY; ANALYSIS 1 AND 2

ANALYSIS 1

$m = .75$

$Y_s = 1.7 \times 10^{-6}$

PASS NUMBER	X_f	X_r	S/F	Q	N_{th}	N_{act}	E*
1	3.55×10^{-4}	3.60×10^{-5}	1.60	1.20	5.15	8	.64
2	4.37×10^{-5}	1.35×10^{-5}	1.53	1.15	2.14	8	.27
3	1.80×10^{-5}	3.90×10^{-6}	1.48	1.12	5.80	8	.73
4	6.50×10^{-6}	2.10×10^{-6}	1.54	1.16	00	8	--

E = .55

ANALYSIS 2

$m = .75$

$Y_s = 8.0 \times 10^{-7}$

PASS NUMBER	N_{th}	N_{act}	E
1	5.07	8	.63
2	1.97	8	.25
3	3.76	8	.47
4	3.10	8	.39

E = .43

*E = N_{th}/N_{act}

necessary to reach .8 ppm acetonitrile versus 1.7 ppm was twenty percent greater.

Analysis 3A, 3B

Determination of the distribution coefficients could introduce large errors in the extractor analysis. Analysis 3A and 3B shown in Table 9, explore the magnitude of error in calculating extractor efficiency introduced by a $\pm$ 10% error in the distribution coefficient's (m) determination. The results are listed below. The percent error given assumes the average distribution coefficient determination is the correct value. For a wt % error in m, a corresponding 33% error in sizing of an extraction is possible here.

m	E	% Error
.83	.36	16
.76	.43	—
.68	.57	33

Analysis 4:

Finally, the extractor's efficiency was analyzed for the acrylonitrile-water-CO_2 system. Here the distribution coefficient was taken at 4.5 due to agreement with previous laboratory results. Once again the amount of acrylonitrile present in the incoming solvent Y_s was determined using the partial pressure method. Y_s was taken as 9.0×10^{-7}. Results from analysis 4 are shown in Table 10. The large reduction in acrylonitrile coupled with a high value of m resulted in an extremely low extractor efficiency. Due to the ease of acrylonitrile extraction, it is recommended here that the extractor design for such a feed be entirely based on the acetonitrile-water-CO_2 equilibrium system.

Commercial Scale Extractor Design

The waste stream tested in the pilot plant was based on a waste stream in the actual industrial process where a 4.8 to 1 dilution (by weight) with water has already taken place. The dilution is performed to prepare the waste for deep well injection. If the waste was not deep well injected, significant economic and environmental gains could be made. This would also mean that the waste could be treated without the 4.8 to 1 dilution. A profile of this new waste stream is given below.

Acetonitrile	1680 ppm
Acrylonitrile	1200 ppm
Ammonium Sulfate	2.0 wt %
Water	97.7 wt %

TABLE 9. EXTRACTOR EFFICIENCY; ANALYSIS 3A AND 3B

ANALYSIS 3A

$m = .83\ (+10\%)$
$Y_s = 8.0 \times 10^{-7}$

PASS NUMBER	X_f	X_r	S/F	Q	N_{th}	N_{act}	E
1				1.33	4.14	8	.52
2				1.27	1.73	8	.22
3				1.23	3.10	8	.39
4				1.28	2.49	8	.31

E = .36

ANALYSIS 3B

$m = .68\ (-10\%)$
$Y_s = 8.0 \times 10^{-7}$

PASS NUMBER	Q	N_{th}	N_{act}	E
1	1.09	6.54	8	.82
2	1.04	2.30	8	.29
3	1.01	5.02	8	.63
4	1.05	4.19	8	.52

E = .57

TABLE 10. EXTRACTOR EFFICIENCY; ANALYSIS 4

ANALYSIS 4

BASIS ACRYLONITRILE-WATER-CO_2 SYSTEM

$m = 4.5$

$Y_s = 9.0 \times 10^{-7}$

PASS NUMBER	X_f	X_r	S/F	Q	N_{th}	N_{act}	E
1	2.77×10^{-4}	2.6×10^{-6}	1.60	7.20	2.33	8	0.291
2	8.8×10^{-6}	2.0×10^{-6}	1.53	6.89	0.73	8	0.091
3	2.8×10^{-6}	1.0×10^{-6}	1.48	6.66	0.55	8	0.068
4	1.0×10^{-6}	1.0×10^{-6}	1.54	6.93	NA	8	

E = 0.15

Basing an extractor design on the results of extracting a more diluted feed is useful due to the ease of extraction of both hazardous organics.

The design was based on the extraction of acetonitrile using a constant distribution coefficient (m = .76), a nearly pure solvent feed ($y_s = 8.0 \times 10^{-7}$), a feed concentration of 1680 ppm acetonitrile and a tray efficiency of .44. The number of theoretical trays was calculated using the Kremser equation. The number of actual trays was calculated by dividing the theoretical tray count by the efficiency. Table 11 shows the results of projecting the actual number of trays necessary to achieve the corresponding levels of acetonitrile in the raffinate.

Analysis 1 uses a solvent-to-feed ratio of 1.5 to 1.0 which is the same as that used in pilot plant runs. Establishing a thirty tray economic cutoff point, the maximum reduction achievable would be from 1680 ppm to less than 50 ppm or 97.0%.

Analysis 2 uses a solvent-to-feed ratio of 2 to 1 which may or may not affect the sieve tray efficiency. If this efficiency holds, one can see that for the same number of trays used in analysis 1, a reduction from 1680 ppm to less than 5 ppm or of 99.7% is achievable.

Analysis 3 examines the effect of $\pm$ 10% error in determining the distribution coefficient on correctly sizing a commercial scale extractor. Distribution coefficients and tray efficiencies based on the pilot plant extraction system data are used to determine the number of theoretical plates and actual plates and are listed in Table 11. From the table, one can see that only a 10% error in distribution coefficient determination can result in as extractor oversizing of greater than 50%. Design work based on pilot plant scale-up must require distribution coefficients to be determined with a high degree of confidence. Also here, the case may be that using a constant distribution coefficient may be a terrible assumption. This would require using more equilibrium points and performing a McCabe-Thiele analysis instead of using the Kremser equation to accurately determine the number of theoretical trays.

Further studies should also concentrate on the validity of the tray efficiency at higher feed concentrations and higher flow rates. The pilot plant extraction took place at only 2 pounds per minute while the commercial scale extractor would be designed for 20 pounds per minute. A more precise determination of the distribution coefficient is also necessary as the design is very sensitive to this parameter.

TABLE 11. COMMERCIAL SCALE EXTRACTION OF ACETONITRILE; DESIGN BASIS, FEED CONCENTRATION OF 1680 PPM

ANALYSIS 1 SOLVENT-TO-FEED RATIO: 1.5 TO 1.0

RAFFINATE (PPM) X_r	N_{th}	N_{act}	REDUCTION % (1 - Xr/Xf)
2	37.1	86	99.9
5	27.5	64	99.7
10	22.2	51	99.4
20	17.3	40	98.8
50	11.6	27	97.0
100	7.8	18	94.1

ANALYSIS 2 SOLVENT-TO-FEED RATIO: 2.0 TO 1.0

RAFFINATE (PPM) X_r	N_{th}	N_{act}	REDUCTION % (1 - Xr/Xf)
2	14.6	34	99.9
5	11.4	27	99.7
10	9.5	22	99.4
20	7.9	18	98.8
50	5.8	14	97.0
100	4.3	10	94.1

ANALYSIS 3 X_r = 5.0 PPM; SOLVENT-TO-FEED RATIO: 1.5 TO 1.0

D.C.	E	N_{th}	N_{act}	RELATIVE % ERROR
.83	.37	20.2	55	20.3
.76	.43	30.3	69	---
.63	.55	57.1	104	50.7

SECTION 6

CONCEPTUAL DESIGN BASED ON DISSOLVED ORGANICS WASTE FEED

BASIS OF DESIGN

Duty of Plant

This extraction plant is designed to process 20 gallons per minute of wastewater. The organics are extracted from the wastewater stream using liquid carbon dioxide solvent. The carbon dioxide is vaporized from the extracted organics, recompressed, liquefied and recycled to the extraction vessel.

The total organics in the feed to the process unit is made up of acetonitrile, acrylonitrile and sulfate salts dissolved in an aqueous stream. Organics will be dissolved by liquid CO_2 and leave the extractor with the extract stream.

Characteristics of Feedstream Recovered Organics Wastewater Effluent

The extraction system is designed to process wastewater streams with properties and compositions at battery limits as shown in the following table:

Feed Rate, GPM	20
Acetonitrile (ppm)	1680
Acrylonitrile (ppm)	1200
Dissolved Sulfates, weight %	2.5
Water, weight %	97.5
Temperature, ^{o}F	80
Specific Gravity	1.0

Characteristics of Recovered Organics

Organics: Acetonitrile, Acrylonitrile weight %	98.5
Carbon Dioxide, weight %	0.5
Water, weight %	1.0
Temperature, ^{o}F	100

Characteristics of Wastewater Effluent

Water, weight %	97.4
Carbon Dioxide, weight %	<0.06
Acrylonitrile (ppm)	<2
Acetonitrile (ppm)	<2
Sulfates, weight %	2.5
Temperature, ^{o}F	100

DESCRIPTION OF PROCESS FLOW

A process flow diagram is presented in Figure 7 for the conceptual design. Wastewater feed is sieved and then pumped to the extractor at about 1100 psig. The feed lines contain strainers to prevent coarse solids from entering the feed pumps and the extractor. Feed enters at the top of the extractor and flows downwards countercurrent to the carbon dioxide (CO_2) solvent stream. The recycled CO_2 enters at the bottom of the extractor and flows up through the column as the dispersed phase.

The extract from the column top section consists of liquid CO_2, and extracted organics. The extraction process is followed by a distillation and evaporation for CO_2 recovery.

The CO_2 extract stream flows through a pressure reducing valve and is fed to a distillation and stripping system for the separation of CO_2 from the organics.

An important feature of the carbon dioxide distillation and stripping is that the bulk of the CO_2 in the extract stream is separated from the product organics stream at high pressure. This minimizes the compression work needed for recycling the CO_2 to the extractor.

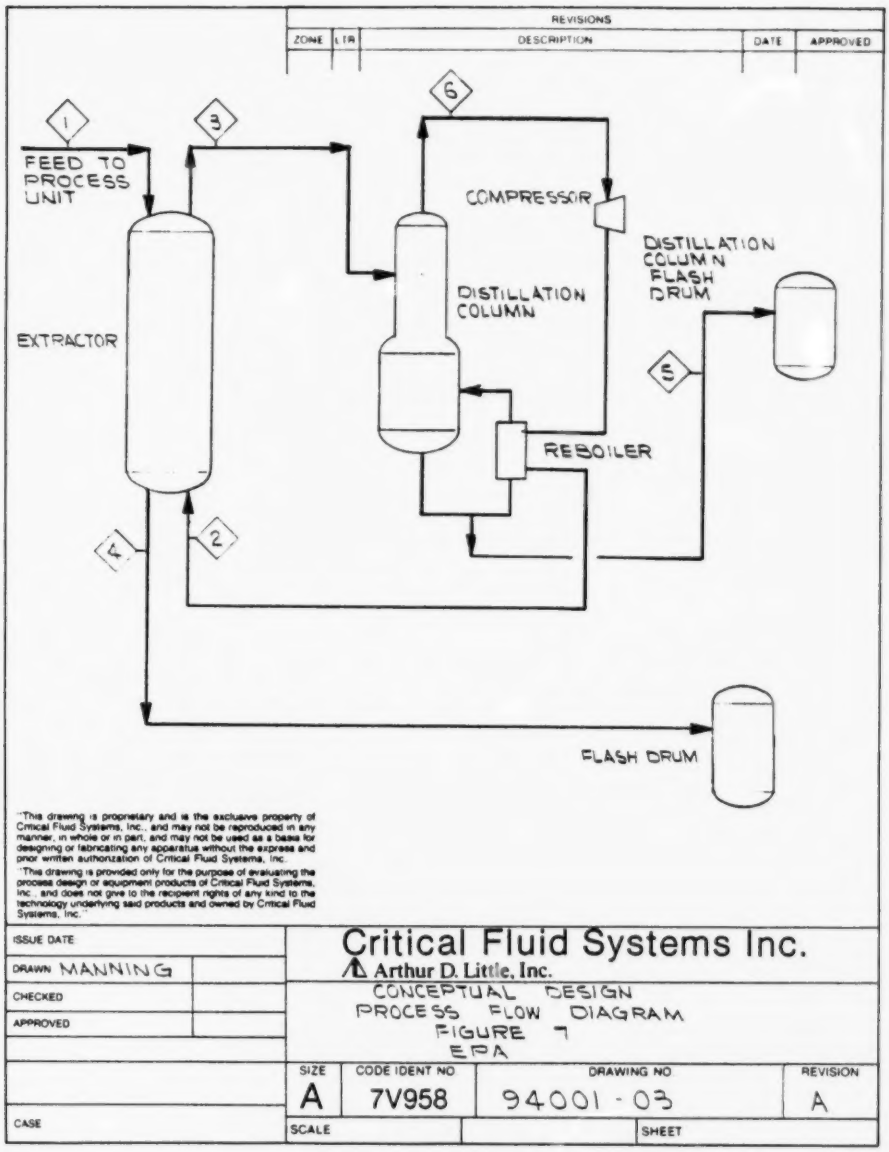
The CO_2 separation is accomplished in a distillation column. The heat of vaporization is supplied from the hot compressed CO_2 vapor discharged from the main compressor. This stream gives up its sensible heat of cooling and liquefaction as it cools from the vapor stage, through the supercritical region and into the liquid phase region.

The organics-rich bottoms then leaving the distillation column is flashed across a pressure reducing valve and flows into a vapor separation drum. The flashed CO_2 vapor is vented and recompressed for recycling. The recovered organics from the bottom of the flash tank flow to off-site disposal.

A cascaded pressure let-down system of flash evaporations is used to recover CO_2 from the raffinate stream. The CO_2 vapors from the raffinate flash vessels are also recompressed and recycled.

OPERATING COSTS

Operating costs are based on a 20 gallons per minute feed basis with a solvent to feed ratio of 1.5 to 1.0 and a reflux ratio of 1 to 1. The costs are given on an annual basis with 8000 hours of operation.


REVISIONS
ZONE
LTR
DESCRIPTION
DATE
APPROVED
1
3
6
FEED TO PROCESS UNIT
COMPRESSOR
DISTILLATION COLUMN FLASH DRUM
DISTILLATION COLUMN
EXTRACTOR
5
REBOILER
4
2
FLASH DRUM
"This drawing is proprietary and is the exclusive property of Critical Fluid Systems, Inc., and may not be reproduced in any manner, in whole or in part, and may not be used as a basis for designing or fabricating any apparatus without the express and prior written authorization of Critical Fluid Systems, Inc.
"This drawing is provided only for the purpose of evaluating the process design or equipment products of Critical Fluid Systems, Inc., and does not give to the recipient rights of any kind to the technology underlying said products and owned by Critical Fluid Systems, Inc."
ISSUE DATE
DRAWN MANNING
CHECKED
APPROVED
CASE
Critical Fluid Systems Inc.
Arthur D. Little, Inc.
CONCEPTUAL DESIGN
PROCESS FLOW DIAGRAM
FIGURE 7
ERA
SIZE
A
CODE IDENT NO
7V958
DRAWING NO
94001-03
REVISION
A
SCALE
SHEET

UTILITIES	ANNUAL COST
ELECTRICITY	
175 KW/HR/HR @ $.04/KW/HR	$56,000
WELL WATER	
18 GPM @ $1.50/1000 GAL	12,960
STEAM	
230 LB/HR @ $10.00/1000 LBS	18,400
SOLVENT MAKE-UP	
CARBON DIOXIDE	
15 LB/HR @ $100.00/2000 LB	6,000
LABOR	
1 OPERATOR @ $13.00/HR	104,000
ANNUAL PROCESSING COST	$197,360

MATERIAL BALANCE

Presented in Table 12 is a material balance for the conceptual design. The concentrations of the waste components are listed for the six major process streams. A solvent-to-feed ratio of 1.5 to 1.0 and a total toxic organics level of 4 ppm in the raffinate were used. The temperatures and pressures of the six main process streams are listed as well.

TABLE 12. CONCEPTUAL DESIGN MATERIAL BALANCE

STREAM NAME & NUMBER FLOW lb/hr	1 FEED TO PROCESS UNIT	2 SOLVENT TO EXTRACTOR	3 EXTRACT FROM EXTRACTOR	4 RAFFINATE FROM EXTRACTOR	5 RECOVERY COLUMN BOTTOMS	6 STILL OVERHEAD
ACETONITRILE	17	--	17	2 ppm	17	--
ACRYLONITRILE	12	--	12	2 ppm	12	--
WATER	9721	--	8	9713	8	--
AMMONIUM SULFATE	250	--	--	250	--	--
CARBON DIOXIDE	--	15000	14437	563	40	30000
TOTAL	10000	15000	14474	10526	77	30000
TEMPERATURE, ^{o}F	80	80	80	80	60	60
PRESSURE, PSIA	1100	1100	1085	1100	750	750

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3. DOE/CS/4025-T1 Critical-Fluid Extraction of Organics from Water, Volumes I and II, June, 1984.

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APPENDIX A

QUALITY CONTROL EVALUATION REPORT

SUMMARY

Purpose of Project

The purpose of this project was to evaluate the feasibility of using near critical carbon dioxide as a solvent to extract hazardous organics from industrial waste samples. Preliminary engineering data could then be provided which would be necessary to design and operate a full scale plant. The hazardous aqueous waste chosen for study and the preparation of a conceptual design was from an acrylonitrile manufacturing plant. The waste contained acrylonitrile (250 ppm), acetonitrile (350 ppm), ammonium sulfate (2.0 wt. %), and water (97.9%). The tests focused on the extractability of the acetonitrile and acrylonitrile from the aqueous feed.

Purpose of Quality Control Evaluation Report (Q.C.E.R.)

This appendix comprises a Q.C.E.R. on the above mentioned project. It reports on the data quality and research results in terms of precision, accuracy, completeness, reproducibility, as well as a semi-quantitative assessment of results and conclusions. Table 1 lists the six major areas where error could have been introduced during experimentation. Errors in accuracy and precision were determined for each parameter.

SOLVENT FLOW RATE

Method of Determination

Liquid carbon dioxide flow rates were measured with a mass flowmeter. The flow meter was calibrated before experimentation with liquid water instead of liquid carbon dioxide which may introduce a slight error in flow measurements. A volume of water was passed through the meter, collected and weighed. The meter displayed a total mass for the water which had passed through it. Calibration of the meter to match the two flows was required. Solvent flow rates could then be read directly from the flow meter.

Analysis of Error

Error in Accuracy

Table 2 lists two reliability runs recorded after calibration was finally set on the mass flowmeter. The error in accuracy was an average 2.9 percent, much of which could

TABLE A-1 EXPERIMENTAL ERRORS

DATA COLLECTED	UNITS	METHOD OF DETERMINATION	RELIAB. TEST	ERROR IN ACCURACY %	ERROR IN PRECISION %
1. SOLVENT FLOWRATE	LB/MIN	MEASUREMENT BY MASS FLOWMETER	CALIBRATION W/WATER, MANUF. SPEC.	+ 2.9	+ 7.7
2. FEED FLOW RATE	LB/MIN	WEIGHING ON BALANCE/STOPWATCH	CALIBRATION, MANUF. SPEC.	+ 1.0	+ 13.5
3. PROCESS PRESSURE	PSIG	GAUGE ON TOP OF EXTRACTOR & STILL	TEMPERATURE AT EQUILIBRIUM, ENTHALPY DIAGRAM	+ 0.5	+ NA
4. PROCESS TEMPERATURE	^{o}F	THERMOCOUPLE	THERMOMETER, ICEBATH	+ 5.3	+ 4.6
5. ORGANIC POLLUTANT LEVELS IN FEED AND RAFFINATE SAMPLES	MASS PERCENT	GAS CHROMATOGRAPHY	BALANCE CALIBRATION AND SUBSEQUENT INVESTIGATION USING PREPARED STANDARDS	+ 0.6-137.**	+ 13.5
6. FEED & RAFFINATE SAMPLING*	NOT APPLICABLE	TAP DIRECTLY INTO PROCESS STREAMS	ANALYTICAL SOLUTION	NEGLIGIBLE	NEGLIGIBLE

*NA - DATA NOT AVAILABLE
**AVERAGE ERRORS ARE USED EXCEPT HERE WHERE A RANGE IS PRESENTED

TABLE A-2 SOLVENT FLOW RATE ANALYSIS;
MASS FLOWMETER CALIBRATION DATA

ERROR IN ACCURACY

TEST NO.	ACTUAL FLOW (LB)	MEASURED FLOW (LB)	%ERROR
1	5.68	5.37	5.5
2	5.71	5.82	1.9
3	5.46	5.53	1.3

ERROR IN ACCURACY = 2.9%

ERROR IN PRECISION 1 LB ACTUAL FLOW BASIS

TEST NO.	ACTUAL FLOW (LB)	MEASURED FLOW (LB)
1	1.00	.95
2	1.00	1.02
3.	1.00	1.01
		X .99
		S.D .04

ERROR IN PRECISION = $\leq$ 7.7%

be attributed to the balance used and to the transfer of water from the flowmeter to the collection vessel. Data point one is suspect and may have been taken before final calibration adjustments were made. The formula used throughout this report for the error in accuracy is given below:

$$\% \text{ Error in Accuracy} = \frac{\text{Experimental Value - Actual Value}}{\text{Actual Value}} \times 100$$

Error in Precision

Table 2 also lists the same reliability runs from which a three point average can give a somewhat meaningful mean value and standard deviation. The water was gravity fed to the meter, so that flow rates probably varied. For this reason, the flow measured was put on one pound actual flow basis. The error in precision calculated in this manner was less than 7.7% with a 95% confidence level. The formulas for calculating the error in precision used throughout this report are given below:

$$X = \left(\sum_{i=1}^{N} X_i\right) / N$$

$$S.D. = \left(\frac{1}{N-1} \sum_{i=1}^{N} (X_i - X)^2\right)^{1/2}$$

where N = Total number of events or measurements
X_i = Experimental values
X = Mean
S.D. = Standard deviation

$$\% \text{ Error in Precision} \quad \frac{2 \times S.D.}{X} \times 100$$

With a 95% level of confidence

FEED FLOW RATE

Method of Determination

Feed flow rates were measured by weight difference on a platform balance scale over fifteen minute time intervals. The scale was zeroed and calibrated by checking with standards of known weight.

Analysis of Error

Error in Accuracy

This error would be directly attributed to the accuracy of the scale which is ± 1%.

Error in Precision

The error which occurred here was due to the pump which probably varied in output. Table 3 lists the actual flow rates measured for one pump setting for all four passes of a multipass extraction experiment. The error in precision calculated with this data was less than 14.0% with a 95% level of confidence.

The solvent flow rate error in precision was not calculated in this manner due to the size of the solvent storage tank (6 tons), which precluded any solvent weight loss measurements.

TABLE A-3 FEED FLOW RATE ANALYSIS, ERROR IN PRECISION
MULTIPASS EXTRACTION DATA EPA 4

PASS NO.	TIME HR:MIN	FEED RATE LB/MIN	AVERAGE FEED RATE (LB/MIN)
1	8:00-8:15	1.66	
	8:15-8:30	1.47	
	8:30-8:45	1.47	
	8:45-9:00	1.47	1.52
2	9:00-9:15	1.47	
	9:15-9:30	1.40	
	9:30-9:45	1.60	1.49
3	9:45-10:00	1.50	
	10:00-10:15	1.47	
	10:15-10:30	1.66	1.54
4	2:25-2:35	1.60	
	2:35-2:45	1.30	
	2:45-2:55	1.60	
	2:55-3:05	1.45	
	3:05-3:15	1.65	1.52
		X	1.51
		S.D.	0.11

ERROR IN PRECISION = 13.9%

PROCESS PRESSURE

Method of Determination

Process pressures were read directly from gauges placed on the top of both the extractor and distillation columns. Reliability tests were conducted on these two gauges due to the critical nature of pressure readings in a near critical process. A calibration check was conducted in the following manner: Liquid carbon dioxide was fed into the extractor/distillation column complex and then sealed off. Given the existing equilibrium between the vapor and liquid phases present, the temperature recorded by the thermocouples in the vessels would give the vapor pressure of the carbon dioxide in the system. The vapor pressure for CO_2 at equilibrium at a given temperature could also be read off of a temperature, entropy diagram which was considered the actual pressure value. The difference between the pressure read from the gauge (experiment) and the temperature entropy chart (actual) was used to determine the gauges error.

Analysis of Error

Error in Accuracy

Table 4 lists the results from the method of calibration described in Section 1. The pressures from the temperature entropy diagram had to be converted to gauge by subtracting 14.7 psi. Reading of the temperature entropy diagram at the temperature given introduced some error itself. But adding an additional $\pm$ 10 psi error in the reading of the chart only would increase the error in accuracy to $\pm$ 1.5% which will be used.

Error in Precision

Due to pressure fluctuations during runs, experimental data could not be used to determine the error in precision. Therefore, an error in precision could not be determined.

TABLE A-4 PRESSURE GAUGE ANALYSIS; ERROR IN ACCURACY

	TEMPERATURE (^{o}F)	PRESSURE GAUGE	ACTUAL	% ERROR
EXTRACTION COLUMN	75	900	900	0
DISTILLATION COLUMN	77	910	915	0.5

PROCESS TEMPERATURE

Method of Determination

Temperatures were recorded by reading directly off of inline thermocouples. A total of twenty four thermocouples are placed throughout the pilot plant to monitor vital temperatures in the process. Twenty two of these were reliability tested by disconnection and placement in an ice water bath with results shown in Table 5. Temperatures recorded by digital readout were compared to temperatures measured with a mercury thermometer.

Analysis of Error

Error in Accuracy

The actual temperature of the ice bath the thermocouples were placed in was measured by a mercury thermometer at 32°F. The average error in accuracy based on the twenty two thermocouples and an actual temperature of 32°F was 5.3%. The maximum error recorded at 18.8% which was from thermocouple 2-2 which records the temperature of the stream flowing into the reboiler. The working condition of this thermocouple was suspect and was replaced.

Error in Precision

Thermocouple #2-10 was chosen at random to perform an error in precision determination and was considered standard for all twenty four, which probably introduces some error itself. The reading was repeated five times with placement of the thermocouples in hot water between readings. Table 5 lists these results. Less than 4.6% error in precision was found at a 95% level of confidence.

Both of the above analyses were subject to the introduction of error in temperature variations in the ice bath itself. To avoid variations, the bath was kept small, full of fresh ice and well stirred before each reading was taken.

FEED AND RAFFINATE CONCENTRATIONS

Method of Determination

Organic solute concentrations in the feed and raffinate were determined using a gas chromatograph. Standards of known solute concentrations were run to generate a standard curve of area versus concentration. Using an area generated at the given elution time for that solute, one could estimate the concentration of that solute in the sample injected.

TABLE A-5 PROCESS TEMPERATURE ANALYSIS

ERROR IN ACCURACY

THERMOCOUPLE NO.	READING (^{o}F)	ACTUAL (^{o}F)	ERROR IN ACCURACY %
3	33	32	3.1
5	30	32	6.3
6	32.5	32	1.6
1-1	32	32	0
1-2	34	32	6.3
1-3	35	32	9.4
1-4	33.5	32	4.7
1-5	35	32	9.4
1-6	34	32	6.3
1-7	33	32	3.1
1-8	34.5	32	7.8
1-9	33	32	3.1
2-1	31	32	3.1
2-2	38	32	18.8
2-3	32	32	0
2-4	30	32	6.3
2-5	31.5	32	1.6
2-6	30	32	6.3
2-7	33	32	3.1
2-8	32	32	3.1
2-10	32	32	0
2-11	32	32	0

ERROR IN ACCURACY = 5.3%

ERROR IN PRECISION

THERMOCOUPLE NO.	TRIAL NO.	READING ^{o}F
2-10	1	32.5
	2	32
	3	33
	4	32
	5	31
	X	32.1
	S.D.	0.7

ERROR IN PRECISION = 4.6%

Injections were made using the same technique every time to minimize sampling error. Care had to be taken to remove all air bubbles from the syringe before injection so that the volume of injection was always constant. Injections for each sample were repeated to insure the validity of individual injections. Blanks were run throughout the analysis to insure that carryover from a previous injection was not a source of error. Rinsing of the syringe with water was carried out when switching from one sample to the next to avoid carryover of solute.

Standards can be prepared by weighing a tare, adding a weight of solute, noting the weight and finally, adding water and noting the final weight. In Table 6, standards number 1 and 5 were prepared in this fashion. A more accurate method of preparing standards of low solute concentration is to dilute a more concentrated standard by the addition of a known weight of water. Standards numbers 2 through 4 were prepared in this fashion by diluting standard number 1.

Analysis of Error

Error in Accuracy

Table 6 lists the concentrations determined from preparations of standards and the corresponding gas chromatograph response areas for the two hazardous solutes, acrylonitrile and acetonitrile. The error in accuracy can be determined by taking four points of the five, performing a linear regression and from this curve estimating a concentration for the fifth which can be compared to the fifth's actual concentration. This can be repeated to find an error in accuracy for each point which are shown on Table 7. The first observation one can make is that an average error in accuracy is meaningless. The second is that accuracy decreases as one approaches the 10 ppm order of magnitude.

TABLE A-6 FEED AND RAFFINATE CONCENTRATION DATA

STANDARD NO.	CONCENTRATION (PPM)		G.C. AREA	
	ACETONITRILE	ACRYLONITRILE	ACETONITRILE	ACRYLONITRILE
1	5320	6520	3.27	4.79
2	476	583	0.294	0.423
3	38.7	47.4	0.0219	0.0314
4	4.9	6.0	0.0027	0.0038
5	261	320	0.156	0.225

TABLE A-7 FEED AND RAFFINATE CONCENTRATION ANALYSIS; ERROR IN ACCURACY

		ACETONITRILE			ACRYLONITRILE		
STANDARD NO.	CORRELATION COEFFICIENT	ACTUAL (PPM)	CALCULATED (PPM)	% ERROR	ACTUAL (PPM)	CALCULATED (PPM)	% ERROR
1	.999	5320	5290	0.6	6520	6610	1.2
2	.999	476	482	1.3	583	582	0.2
3	.999	38.7	37.5	3.2	47.4	50.3	6.1
4	.999	4.9	7.1	44.9	6.0	14.2	137.
5	.999	261	254	2.6	320	310	3.1

The error in accuracy for standard number 4 in this analysis was exactly equal to the deviation of the curve from a Y-intercept of zero. For low ppm measurements in the future, it is suggested that more standards be run in this range and a separate curve be generated for data analysis.

Error in Precision

A standard was prepared containing 261 ppm of acetonitrile and 320 ppm of acrylonitrile. This standard was then injected into the gas chromatograph a total of nine times. Response areas were recorded, averaged and a standard deviation was calculated as shown in Table 8. The error in precision was less than or equal to 13.5% with a 95% level of confidence.

TABLE A-8 FEED AND RAFFINATE CONCENTRATION ANALYSIS; ERROR IN PRECISION

INJECTION NO.	ACETONITRILE AREA (261 PPM)	ACRYLONITRILE AREA (320 PPM)
1	.172	.254
2	.200	.286
3	.199	.282
4	.199	.282
5	.197	.276
6	.194	.275
7	.170	.241
8	.185	.259
9	.205	.294
X	.191	.272
S.D.	.0127	.0172
ERROR IN PRECISION	13.3%	12.6%

FEED AND RAFFINATE SAMPLING

Method of Determination

Feed samples were drawn every fifteen minutes from a line between the feed tanks and the feed pump. Samples were collected by injection with a syringe into an evacuated tube. This enabled sampling to be done without exposure to the toxic chemicals present. It also allowed for the drawing of samples with very little vapor space present which could affect laboratory analysis. Samples were labeled by experimental run and given a feed number corresponding to a time period noted in the run charts.

Raffinate samples were drawn from a pressure let-down vessel which allowed for the venting of carbon dioxide from the samples. These samples were also taken every fifteen minutes and labelled in a similar fashion.

Analysis of Error

The error in sampling may be complicated by outside factors such as incomplete mixing in the feed tanks, sampling technique, laboratory analysis, and solvent and feed flow rates. Assuming these errors except that due to gas chromatography are negligible, one can analyze the maximum error of sampling by examining the deviation from one sample to the rest of solute concentration.

Error in Precision

Table 9 lists the error in precision calculations for sampling. Once again, one sees that at low concentrations, the error in sampling is magnified greatly. If one subtracts the error in precision from the feed concentration determination (see Table 8) which is at the same range of concentration as Pass #1 in Table 9, then one sees that the sampling error comes up negative. This is a good indication that the error in precision in sampling is negligible.

Error in Accuracy

This error is essentially negligible in view of the above results. The error in accuracy would be obscured by the error of feed and raffinate concentration determination.

TABLE A-9 FEED AND RAFFINATE SAMPLING ANALYSIS; ERROR IN PRECISION

PASS NO.	FEED NO.	GAS CHROMATOGRAPH AREA ACETONITRILE	ACRYLONITRILE
1	2	.233	.208
	3	.252	.227
	4	.251	.224
	5	.231	.204
X		.242	.216
S.D.		.0112	.0117
% ERROR		9.3%	10.8%
2	7	.0305	.0051
	8	.0305	.0048
	9	.0318	.0050
X		.0309	.0050
S.D.		.0008	.0002
% ERROR		5.2%	6.1%
3	10	.0122	.0013
	11	.0127	.0018
	12	.0136	.0016
	13	.0125	.0015
X		.0128	.0016
S.D.		.0006	.0002
% ERROR		9.4%	26.0%
4	15	.0041	ND*
	16	.0044	ND
	17	.0041	ND
	18	.0058	ND
X		.0046	---
S.D.		.0008	
% ERROR		35.3%	

*ND - Non-detectable, i.e. no gas chromatograph response

APPENDIX B

TABLE B-1 ENGLISH TO METRIC CONVERSION TABLE

TO CONVERT FROM	TO	MULTIPLY BY
FT	METER	0.305
GAL	LITER	3.785
GAL/HR	LITER/HR	227.1
GAL/MIN	LITER/HR	3.787
IN	CM	2.540
LB	KG	0.454
LB/MIN	KG/HR	27.24
PSI	N/M^2	4.448